

Kinetic and mechanistic studies
for the molybdenum-catalyzed oxidation
of organic sulfides and olefins by $t\text{-BuO}_2\text{H}$

by

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ABSTRACT

This research was focussed on the effects of light, solvent and substituents in the molybdenum-catalyzed oxidation of phenylmethyl sulfides with $t\text{-BuO}_2\text{H}$ and on the effect of light in the molybdenum-catalyzed epoxidation of 1-octene with $t\text{-BuO}_2\text{H}$.

It was shown that the Mo(CO)_6 -catalyzed oxidation of phenylmethyl sulfide with $t\text{-BuO}_2\text{H}$, at 35°C , proceeds 278 times faster under UV light than under laboratory lighting, whereas the $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation proceeds only 1.7 times faster under UV light than under normal laboratory lighting. The difference between the activities of both catalysts was explained by the formation of the catalytically active species, Mo(VI) .

The formation of the Mo(VI) species, from Mo(CO)_6 was observed from the IR spectrum of Mo(CO)_6 in the carbonyl region.

The Mo(CO)_6 -catalyzed epoxidation of 1-octene with $t\text{-BuO}_2\text{H}$ showed that the reaction proceeded 4.6 times faster under UV light than in the dark or under normal laboratory lighting; the rates of epoxidations were found to be the same in the dark and under normal laboratory lighting.

The kinetics of the epoxidations of 1-octene with $t\text{-BuO}_2\text{H}$, catalyzed by $\text{MoO}_2(\text{acac})_2$ were found to be complicated; after fast initial rates, the epoxidation rates decreased with time.

The effect of phenylmethyl sulfide on the Mo(CO)_6 -catalyzed epoxidation of 1-octene was studied. It was shown that instead of phenylmethyl sulfide, phenylmethyl sulfone, which formed rapidly at 85°C , lowered the reaction

rate. The epoxidation of 1-octene was found to be 2.5 times faster in benzene than in ethanol.

The substituent effect on the $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidations of p-OH, p- CH_3O , p- CH_3 , p-H, p-Cl, p-Br, p- CH_3CO , p-HCO and p- NO_2 substituted phenylmethyl sulfides were studied. The oxidations followed second order kinetics for each case; first order dependency on catalyst concentration was also observed in the oxidation of p- CH_3OPhSMe and PhSMe.

It was found that electron-donating groups on the para position of phenylmethyl sulfide increased the rate of reaction, while electron-withdrawing groups caused the reaction rate to decrease. The reaction constants δ were determined by using σ , σ^- and σ^* constants. The rate effects were paralleled by the activation energies for oxidation.

The decomposition of t-BuO₂H in the presence of $\text{Mo}(\text{CO})_6$, $\text{MoO}_2(\text{acac})_2$ and $\text{VO}(\text{acac})_2$ was studied. The rates of decomposition were found to be very small compared to the oxidation rates at high concentration of catalysis.

The relative rates of the $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of p- NO_2PhSMe by t-BuO₂H in the presence of either p- CH_3OPhSMe or PhSMe clearly show that PhSMe and p- CH_3OPhSMe act as co-catalysts in the oxidation of p- NO_2PhSMe .

Benzene, mesitylene and cyclohexane were used to determine the effect of solvent in the $\text{MoO}_2(\text{acac})_2$ and $\text{Mo}(\text{CO})_6$ -catalyzed oxidation of phenylmethyl sulfide. The results showed that in the absence of hydroxylic solvent, a second molecule of t-BuO₂H was involved in the transition state. The complexation of the solvent with the catalyst could not be explained.

The oxidations of diphenyl sulfoxide catalyzed by $\text{VO}(\text{acac})_2$, $\text{Mo}(\text{CO})_6$ and $\text{MoO}_2(\text{acac})_2$ showed that $\text{VO}(\text{acac})_2$ catalyzed the oxidation faster than $\text{Mo}(\text{CO})_6$ and $\text{MoO}_2(\text{acac})_2$. Moreover, the $\text{Mo}(\text{CO})_6$ -catalyzed oxidation of diphenyl sulfoxide proceeded under UV light at 35°C .

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TABLE OF CONTENTS

	page
Abstract	3
Acknowledgement	5
List of Tables	8
List of Figures	10
List of Appendices	14
List of Abbreviations	14a
Introduction	15
I. Catalysis in hydroperoxide reactions	15
II. Metal-catalyzed reactions of hydroperoxides	17
(a) Homolytic mechanism in metal catalysis	
(b) Heterolytic mechanism in metal catalysis	
III. Activation of catalyst	18
IV. Complexation of catalyst	19
V. Epoxidation of olefins in the presence of metal ion	19
(a) Mechanism of the epoxidation	23
in the presence of vanadium catalyst	
(b) Mechanism of the epoxidation	24
in the presence of molybdenum catalyst	
VI. Epoxidation of allyl alcohol	25
in the presence of metal ion and mechanism of reaction	
VII. Metal-catalyzed oxidation	30
of phosphines, arsines and stibines	
VIII. Metal-catalyzed oxidation of amines and anilines	30
IX. Metal-catalyzed oxidation of organic sulfides	32

	page
Experimental	38
I. Apparatus	38
II. Reagents	38
III. Kinetic studies	48
(a) Oxidation of organic sulfides	48
1. Titrations	
2. Gas chromatographic analysis	
(b) Competition reactions	50
1. gas chromatographic studies	
2. UV spectral analysis	
(c) Oxidation of 1-octene	51
(d) Preparation of IR samples	52
Results and Discussion	53
I. The light effect on reactions	53
II. The epoxidation of 1-octene	65
III. The Mo(CO)_6 -catalyzed epoxidation of 1-octene in the presence of phenylmethyl sulfide	75
IV. The oxidation of phenylmethyl sulfide and substituted phenylmethyl sulfides	79
V. The decomposition of t-butyl hydroperoxide in the presence of transition metal complexes	109
VI. Competitive reactions of p-methoxy-, p-nitro- and unsubstituted phenylmethyl sulfides	114
VII. The solvent effect on the oxidation of phenylmethyl sulfide	120
VIII. The oxidation of diphenyl sulfoxide	128
Conclusion	134
References	136
Appendices	141

LIST OF TABLES

	page
1. Reagents purchased and used	39
2. Mo(CO)_6 -catalyzed oxidation of diphenyl sulfide with $t\text{-BuO}_2\text{H}$ in ethanol	55
3. The oxidation of phenylmethyl sulfide by $t\text{-BuO}_2\text{H}$ in the presence of either Mo(CO)_6 or $\text{MoO}_2(\text{acac})_2$ under various light conditions in ethanol	57
4. The epoxidation of 1-octene by $t\text{-BuO}_2\text{H}$ in the presence of Mo(CO)_6 and $\text{MoO}_2(\text{acac})_2$ under various light conditions	66
5. Carbonyl stretching frequencies of Mo(CO)_6 under different conditions	70
6. Mo(CO)_6 -catalyzed epoxidation of 1-octene by $t\text{-BuO}_2\text{H}$ in the presence of phenylmethyl sulfide	76
7. $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of phenylmethyl sulfide with $t\text{-BuO}_2\text{H}$ in ethanol	80
8. $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of p-methoxyphenylmethyl sulfide with $t\text{-BuO}_2\text{H}$ in ethanol	84
9. $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of p-methylphenylmethyl sulfide with $t\text{-BuO}_2\text{H}$ in ethanol	85
10. $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of p-nitro-, p-chloro-, p-bromo-, p-hydroxyphenylmethyl sulfides and p-methylthiobenzaldehyde with $t\text{-BuO}_2\text{H}$ in ethanol	86
11. Activation energies for the oxidation of phenylmethyl sulfide and p-methoxy-, p-methyl-, p-nitro- and p-acetylphenylmethyl sulfides	98
12. Rates of the decomposition of $t\text{-BuO}_2\text{H}$ in ethanol at 35°C	110
13. The relative rate constants for the oxidation of phenylmethyl sulfide and p-nitrophenylmethyl sulfide and p-methoxyphenylmethyl sulfide and p-nitrophenylmethyl sulfide by $t\text{-BuO}_2\text{H}$ in the presence of $\text{MoO}_2(\text{acac})_2$	114

	page
14. The oxidation of phenylmethyl sulfide with $t\text{-BuO}_2\text{H}$ in the presence of Mo(CO)_6 and $\text{MoO}_2(\text{acac})_2$ in various solvents	121
15. The oxidation of diphenyl sulfoxide with $t\text{-BuO}_2\text{H}$ in the presence of Mo(CO)_6 , $\text{MoO}_2(\text{acac})_2$ and VO(acac)_2 under various light conditions	129

LIST OF FIGURES

	page
1. Second order rate plots for $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of phenylmethyl sulfide with $t\text{-BuO}_2\text{H}$ in ethanol at 35°C , in dark, under 175 W spotlight, and under UV light	59
2. Second order rate plot for $\text{Mo}(\text{CO})_6$ -catalyzed oxidation of phenylmethyl sulfide with $t\text{-BuO}_2\text{H}$ in ethanol at 35°C under UV light	60
3. Second order rate plot for $\text{Mo}(\text{CO})_6$ -catalyzed oxidation of phenylmethyl sulfide with $t\text{-BuO}_2\text{H}$ in ethanol at 35°C under normal light conditions	61
4. Absorbance versus time for the IR band of CO in $\text{Mo}(\text{CO})_6$ (1.82×10^{-3} M) in the presence of 1.115 M $t\text{-BuO}_2\text{H}$ under UV light	63
5. Concentration versus time for the epoxidation of 1-octene with $t\text{-BuO}_2\text{H}$ in benzene in the presence of $\text{Mo}(\text{CO})_6$	67
6. First order rate plots for the epoxidation of 1-octene with $t\text{-BuO}_2\text{H}$ in benzene in the presence of $\text{Mo}(\text{CO})_6$ at 85°C in dark, under normal light condition and under UV light	68
7. First order rate plot for the epoxidation of 1-octene with $t\text{-BuO}_2\text{H}$ in benzene in the presence of $\text{MoO}_2(\text{acac})_2$ at 85°C in dark	72
8. First order rate plot for the epoxidation of 1-octene with $t\text{-BuO}_2\text{H}$ in benzene in the presence of $\text{MoO}_2(\text{acac})_2$ at 85°C under normal light condition	73
9. First order rate plot for the epoxidation of 1-octene with $t\text{-BuO}_2\text{H}$ in benzene in the presence of $\text{MoO}_2(\text{acac})_2$ at 85°C under UV light	74
10. Concentration versus time for the epoxidation of 1-octene with $t\text{-BuO}_2\text{H}$ in benzene in the presence of $\text{Mo}(\text{CO})_6$ and phenylmethyl sulfide at 85°C	77

	page
11. First order rate plot for the epoxidation of 1-octene with t-BuO ₂ H in benzene in the presence of Mo(CO) ₆ and phenylmethyl sulfide at 85°C	78
12. Second order rate plot for the oxidation of phenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 27°C	81
13. The logarithm of the reaction rate versus the logarithm of the catalyst concentration in the MoO ₂ (acac) ₂ -catalyzed oxidation of phenylmethyl sulfide with t-BuO ₂ H in ethanol at 35°C	82
14. Second order rate plot for the oxidation of p-methylphenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 23°C	87
15. Second order rate plot for the oxidation of p-nitrophenylmethyl sulfide with t-BuO ₂ H in the presence of MoO ₂ (acac) ₂ at 60°C	88
16. Second order rate plot for the oxidation of p-chlorophenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 35°C	89
17. Second order rate plot for the oxidation of p-bromophenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 35°C	90
18. Second order rate plot for the oxidation of p-hydroxyphenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 35°C	91
19. Second order rate plot for the oxidation of 4-methylthiobenzaldehyde with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 35°C	92
20. Second order rate plot for the oxidation of p-methoxyphenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 21°C	93
21. Second order rate plot for the oxidation of p-acetylphenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 60°C	94
22. The logarithm of the reaction rate versus the logarithm of the catalyst concentration in the MoO ₂ (acac) ₂ -catalyzed oxidation of p-methoxyphenylmethyl sulfide with t-BuO ₂ H in ethanol at 35°C	95

	page
23. Arrhenius plot for the oxidation of phenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂	99
24. Arrhenius plot for the oxidation of p-methoxyphenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂	100
25. Arrhenius plot for the oxidation of p-methylphenylmethyl sulfide with t-BuO ₂ H in the presence of MoO ₂ (acac) ₂	101
26. Arrhenius plot for the oxidation of p-nitrophenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂	102
27. Arrhenius plot for the oxidation of p-acetylphenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂	103
28. Arrhenius plot for the oxidation of phenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ under UV light	104
29. Arrhenius plot for the oxidation of phenylmethyl sulfide with t-BuO ₂ H in ethanol in the presence of Mo(CO) ₆ under UV light	105
30. Hammett plot for the oxidation of arylmethyl sulfides with t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 35°C	106
31. First order rate plot for the decomposition of t-BuO ₂ H in ethanol in the presence of Mo(CO) ₆ at 35°C	111
32. First order rate plot for the decomposition of t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 35°C	112
33. First order rate plot for the decomposition of t-BuO ₂ H in ethanol in the presence of VO(acac) ₂ at 35°C	113
34. Concentration versus time for the competitive oxidation of p-methoxyphenylmethyl sulfide and p-nitrophenylmethyl sulfide by t-BuO ₂ H in the presence of MoO ₂ (acac) ₂ at 40°C	116

	page
35. Concentration versus time for the competitive oxidation of phenylmethyl sulfide and p-nitrophenylmethyl sulfide by t-BuO ₂ H in ethanol in the presence of MoO ₂ (acac) ₂ at 40°C	117
36. Rate plots for the competitive reactions	118
37. Second order rate plots for the Mo(CO) ₆ -catalyzed oxidation of phenylmethyl sulfide with t-BuO ₂ H at 35°C under normal light conditions, in mesitylene, in benzene, and in cyclohexane	123
38. Second order rate plots for the Mo(CO) ₆ -catalyzed oxidation of phenylmethyl sulfide with t-BuO ₂ H at 35°C under UV light in benzene, in mesitylene and in cyclohexane	124
39. Second order rate plots for the MoO ₂ (acac) ₂ -catalyzed oxidation of phenylmethyl sulfide with t-BuO ₂ H in mesitylene at 35°C under UV light and under normal light conditions	125
40. Second order rate plots for the MoO ₂ (acac) ₂ -catalyzed oxidation of phenylmethyl sulfide with t-BuO ₂ H in benzene at 35°C under UV light and under normal light conditions	126
41. Second order rate plots for the VO(acac) ₂ -catalyzed oxidation of diphenyl sulfoxide with t-BuO ₂ H in ethanol at 35°C under normal light conditions and under UV light	130
42. Second order rate plot for the MoO ₆ -catalyzed oxidation of diphenyl sulfoxide with t-BuO ₂ H in ethanol at 35°C under UV light	131
43. Second order rate plots for the MoO ₂ (acac) ₂ -catalyzed oxidation of diphenyl sulfoxide with t-BuO ₂ H in ethanol at 35°C in dark, under normal light conditions, and under UV light	132

LIST OF APPENDICES

	page
1 The chromatogram and the mass spectra of the mixture of ethanol, triethylphosphite, triethylphosphate, diphenyl sulfide and diphenyl sulfoxide	142
2 The chromatograms of the samples of the competitive reaction mixture	146
3. Extinction coefficients for methyl sulfoxide, p-nitrophenylmethyl sulfide and p-nitrophenylmethyl sulfoxide	149
4. IR spectrum of Mo(CO)_6 in ethanol at 20°C	152
5. IR spectra of Mo(CO)_6 in the presence of t-BuO ₂ H in ethanol at 20°C at 0-30 minutes	154
6. IR spectra of Mo(CO)_x -1-octene under various conditions and 1-octene in the region of 2100-1700 cm^{-1}	160

LIST OF ABBREVIATIONS

acac	= acetylacetonate
dpm	= dipivaloylmethide
hfac	= hexafluoroacetylacetonate
HP	= hydroperoxide
naph	= naphthenate
hmpa	= hexamethylphosphorous triamide
oct	= octanate
dien	= diethylene triamine

INTRODUCTION

I. Catalysis in hydroperoxide reactions

The catalytic activity of the transition metal acetylacetonates (Cr^{3+} , V^{3+} , VO^{2+} , MoO_2^{2+} , Co^{3+} , Cu^{2+} , Co^{2+} , Mn^{3+} , Mn^{2+} , Al^{3+} , Fe^{3+} , Mg^{2+} , Ni^{2+} , TiO_2^{2+} , Zn^{2+} , Zr^{4+}) were investigated in the epoxidation of 2,4,4-trimethyl-1-pentene with $t\text{-BuO}_2\text{H}$ (1). It was shown that Cr^{3+} , MoO_2^{2+} , VO^{2+} , V^{3+} compounds gave good yields of the epoxide. Other metals gave either poor or no yields of the epoxide, due to the decomposition of $t\text{-BuO}_2\text{H}$.

Sheng and Zajacek (2) have studied the effectiveness of the following transition metal complexes in the epoxidation of 2-methyl-2-pentene with $t\text{-BuO}_2\text{H}$:

Sodium molybdate, sodium tungstate, sodium vanadate, molybdenum sulfide, molybdenum dioxide, molybdenum trioxide, silicomolybdic acid, phosphomolybdic acid, phosphomolybdic acid + sodium molybdate, sodium silico-12-molybdate + sodium molybdate, sodium phospho-12-molybdate, sodium phospho-12-molybdate + sodium molybdate, sodium phospho-18-molybdate, sodium phospho-18-molybdate + sodium molybdate, ethylphosphomolybdate + sodium molybdate, monoethyl-dihydrophosphomolybdate + sodium molybdate, molybdenum dioxyacetylacetonate, molybdenum hexacarbonyl, molybdenum hexacarbonyl + sodium molybdate, molybdenum pentachloride, vanadium oxyacetylacetonate, manganous acetylacetonate, ferric acetylacetonate, cobaltic acetylacetonate, rhodium chloride, nickel acetylacetonate, potassium platinous chloride, tetrammine copper(II)

sulfate, potassium gold cyanide. Of these complexes, Mo(CO)_6 and $\text{MoO}_2(\text{acac})_2$ were found to be the most effective catalysts.

Sheldon (3) has shown that Mo(CO)_6 , W(CO)_6 and $\text{MoO}_2(\text{acac})_2$ are the best homogeneous catalysts. and TiO_2 on SiO_2 the best heterogeneous catalysts among the following complexes in the epoxidation of cyclohexene with $t\text{-BuO}_2\text{H}$: Mo(CO)_6 , $\text{MoO}_2(\text{acac})_2$, W(CO)_6 , WO(acac)_2 , TiO_2 on SiO_2 , Ti(OBu)_4 , TiO(acac)_2 , UO(acac)_2 , $\text{UO}_2\text{Cl}_2(\text{hmpa})_2$, $\text{UO}_2(\text{acac})_2$, Cr(acac)_2 , Nb(OBu)_5 , Ta(OBu)_5 , Zr(acac)_4 , Th(acac)_4 , Zr(OPr)_4 , SeO_2 and SnO_2 .

The role of the catalyst in the epoxidation reaction is explained by two factors. The first is the Lewis acidity of the catalyst, which withdraws electrons from the peroxidic oxygen of the hydroperoxide, making it more susceptible to attack by nucleophiles. Lewis acidity of metal complexes increases with increasing oxidation state of the metal. In agreement with this theory, catalytically active species were found to be Mo(VI) , W(VI) , V(V) and Ti(IV) .

The second factor is the oxidation potential of the catalyst, i.e., if the metal is a strong oxidant, it will cause decomposition of the hydroperoxide. If it is a weak oxidant, it behaves as a catalyst.

On the basis of these two factors, the higher activity of Mo(VI) compared with Cr(VI) can be explained. Both are good Lewis acids, but Cr(VI) is also a strong oxidant, and causes decomposition of the hydroperoxide. Also, non-transition elements such as SeO_2 , B_2O_3 and SnO_2 are as acidic as MoO_3 , but their strong oxidative properties cause decomposition of the hydroperoxide.

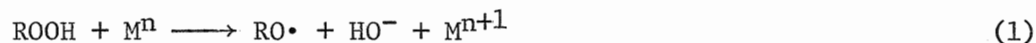
II. Metal-catalyzed reaction of hydroperoxides

The metals which catalyze reactions of hydroperoxides can be divided into two groups. The first group, Co, Mn, Fe, Cu and Al, facilitates homolysis of the O-O bond by having close-lying oxidation states. The second group includes metals such Mo, V and W which, in their high oxidation states, can facilitate heterolysis of the O-O bond.

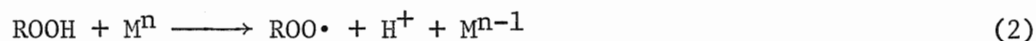
(a) Homolytic mechanism in metal catalysis

Homolytic decomposition of hydroperoxides by metal ions can be divided into three groups:

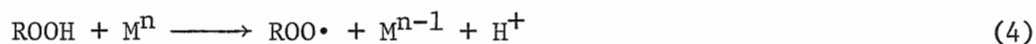
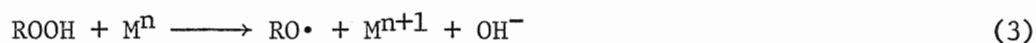
1. Reductive cleavage of hydroperoxide is depicted by the reaction



2. Oxidative cleavage is represented as



3. Catalytic redox cleavage involves both oxidative and reductive cleavage



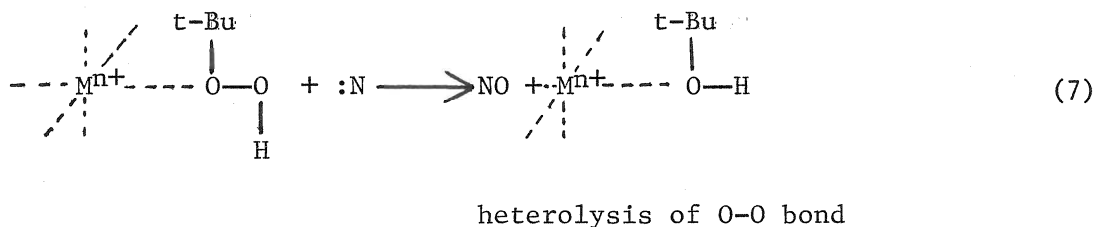
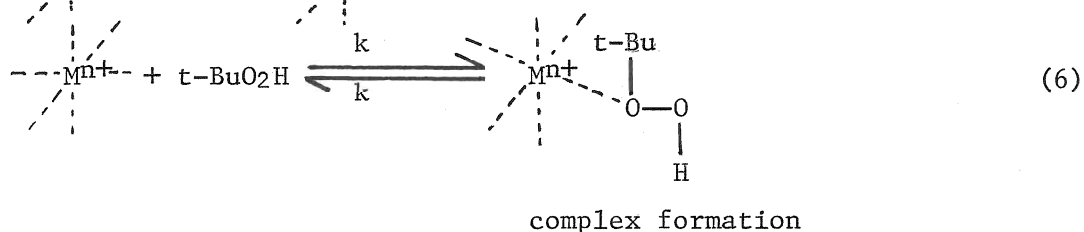
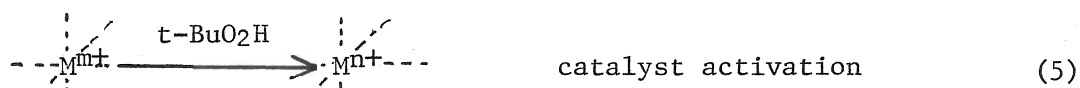
Co and Mn are the most effective autoxidation catalysts.

(b) Heterolytic mechanism in metal catalysis

Metal catalyzed heterolytic reactions of hydroperoxides were studied for a wide range of organic substrates in the presence of active Mo(VI), V(V), Cr(VI) and W(VI) species. The active oxidizing agent is the complex of the hydroperoxide with the catalyst in its highest oxidation state. This means that complexes such as $\text{Mo}(\text{CO})_6$, Mo^0 , $\text{W}(\text{CO})_6$, W^0 ;

$\text{VO}(\text{acac})_2$, V^{4+} , are oxidized by hydroperoxide to their

high oxidation states Mo(VI), W(VI) and V(V) respectively, and that these species form complexes with the hydroperoxide (2).



III. Activation of catalyst

The conversion of Mo^{5+} oxidation state by ethylbenzene hydroperoxide to Mo^{6+} oxidation state was observed by ESR studies (4). ESR signals of the molybdenum resinate (Mo^{5+}) in ethyl benzene decreased with the addition of ethylbenzene hydroperoxide. This observed decrease was related to a redox process.

Similar studies were done with $\text{VO}(\text{acac})_2$ (5). The UV-visible spectrum of $\text{VO}(\text{acac})_2$ in ethanol gave maxima at 775 and 580 nm. These were attributed to d-d transition of this complex. After addition of excess $\text{t-BuO}_2\text{H}$ to $\text{VO}(\text{acac})_2$ solution, both maxima disappeared. This clearly showed that V^{4+} was converted to V^{5+} by removing one electron from the d orbital.

Similarly, the ESR spectrum of $\text{VO}(\text{acac})_2$ in ethanol showed eight resonance lines which disappeared after addition of excess $\text{t-BuO}_2\text{H}$. The half-life of the V (IV) species was estimated to be 20 s.

IV. Complexation of catalyst

The formation of HP-metal complex was studied for MoO_2^{2+} , VO^{2+} acetylacetonate and molybdenum(dioxo-bis-1,2-cyclohexanediolate) by Svitych (6, 7) and Skibida (8) in their NMR work.

In the presence of these complexes, the NMR signal of the protons of the OH group of $t\text{-BuO}_2\text{H}$ is shifted and broadened because of complexation.

V. Epoxidation of olefins in the presence of metal ions

The kinetic and mechanistic studies of the epoxidation reactions of olefins with different hydroperoxides in the presence of molybdenum and vanadium catalysts have been reported (2, 9-23).

The epoxidation of 1- and 2-octene with $t\text{-BuO}_2\text{H}$ in the presence of $\text{Mo}(\text{CO})_6$ have been studied by Sheng and Zajacek (2). Kinetics of the reaction showed that the epoxidation reaction is first order in olefin, in $t\text{-BuO}_2\text{H}$, and in $\text{Mo}(\text{CO})_6$. The rate expression is given by

$$\text{Rate} = k[\text{olefin}][t\text{-BuO}_2\text{H}][\text{Mo}(\text{CO})_6] \quad (8)$$

The same reaction in different atmospheres showed that oxygen does not lower the reaction rate, but reduces the life of the catalyst, whereas carbon monoxide reduces the rate of reaction. The conversion of hydroperoxide was 54% and 31% in one hour at 90°C under nitrogen and carbon monoxide atmospheres, respectively.

Electron donating groups around the double bond and electron withdrawing groups on the para position of cumene hydroperoxide increased the rate of reaction.

The decomposition of hydroperoxide was insignificant when the reaction was run in a large excess of olefin. In the absence of olefin, 6.2% of hydroperoxide decomposed in one hour in benzene at 87°C.

The epoxidation of cis- and trans-2-butene with cumene hydroperoxide gave cis- and trans-epoxide, respectively. This shows that the reaction is stereospecific.

The same authors (9) have reported that the epoxidation of 1,4-hexadiene with t-BuO₂H in the presence of Mo(CO)₆ gave predominantly the internal epoxide. When the pure cis- and trans-1,4-hexadiene were reacted separately, the ratio of internal epoxide to external epoxide was 11:1 for the cis isomer and 6:1 for the trans isomer.

V(oct)₃, VO(acac)₂, V(acac)₃ were used as catalysts in the epoxidation of cyclohexene with t-BuO₂H by Gould et al. (10). They showed that the reaction is first order in catalyst in the range of 6×10^{-5} to 1.2×10^{-3} M of VO(acac)₂, also first order in cyclohexene within the range 0.0875 M to 1.795 M. Dependence of hydroperoxide concentration is analogous to Michaelis-Menten type enzyme catalysis. The co-product t-BuOH inhibits the reaction rate by forming V-alcohol and V-(alcohol)₂ complexes.

Kinetic and mechanistic studies of the epoxidation of cyclohexene and cyclooctene with t-BuO₂H in the presence of VO(acac)₂, VO(dpm)₂, VO(hfac)₂ and MoO₂(acac)₂ were reported in a work of E. S. Gould and coworkers (11). Their kinetic observations are consistent with the formation of the vanadium(V)-hydroperoxide complex in the vanadium catalyzed systems. In the molybdenum catalyzed systems, the formation of molybdenum-hydroperoxide, molybdenum-olefin and molybdenum-hydroperoxide-olefin complexes are also

consistent with the kinetic data. The association constants of these molybdenum complexes were found to be $K_{\text{Mo-HP}} = 21.3$, $K_{\text{Mo-ol}} = 6.22 \text{ M}^{-1}$ and $K_{\text{Mo-HP-ol}} = 0.26 \text{ M}^{-2}$. The existence of the ternary complex, Mo-HP-ol, does not mean that the epoxidations pass specifically through the Mo-HP-ol complex. There is a contribution of each complex to the rate determining step.

According to activation parameters for $\text{VO}(\text{acac})_2$, $\text{VO}(\text{dpm})_2$, $\text{VO}(\text{n-BuO})_3$ and $\text{VO}(\text{hfac})_2$, catalyzed epoxidation of cyclohexene indicates that these catalysts retain, at least in part, when their environment converted to catalytically active species V(V) , although the rate constants are not greatly different. Furthermore, the V-HP complex is more stable with fluorinated complexes of vanadium acetylacetonate than $\text{VO}(\text{acac})_2$ and $\text{VO}(\text{dpm})_2$, in which the metal centers are less electrophilic.

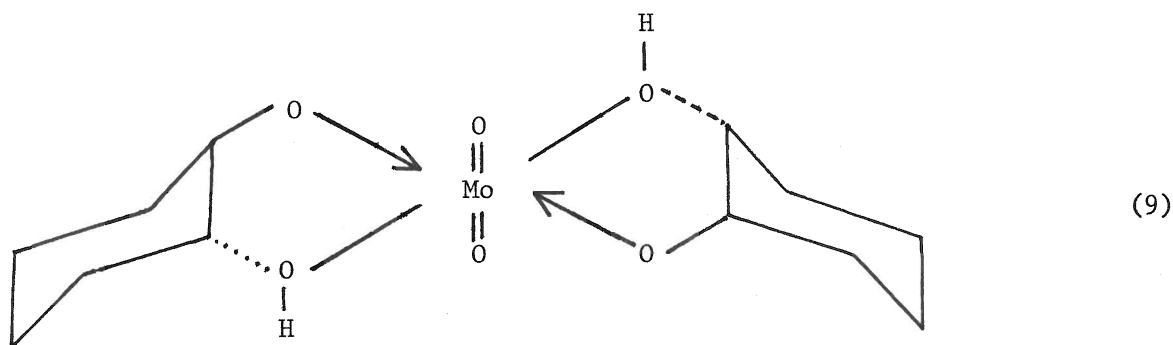
Addition of $t\text{-BuOH}$ reduced the epoxidation rate by half when the ratio of $t\text{-BuO}_2\text{H}$ to $t\text{-BuOH}$ was 1:10.

As in a previous study (10), the vanadium catalyzed reaction is first order in olefin and in catalyst, but showed a Michaelis-Menten type dependency on hydroperoxide concentration.

$\text{MoO}_2(\text{acac})_2$ had a reaction rate of 100 times faster than the aforementioned vanadium complexes. The kinetics of the molybdenum-catalyzed reaction was found to be complicated.

Sheldon (12) had shown that the nature of the ligand has an effect on the catalytic activity of Mo(VI) complexes. The final epoxidation rates of cyclohexene with $t\text{-BuO}_2\text{H}$ in the presence of Mo(CO)_6 , $\text{MoO}(\text{acac})_2$,

$\text{MoO}_2(\text{propane-1,2-diol})_2$, $\text{MoO}_2(\text{trans-cyclohexane-1,2-diol})_2$, $\text{MoO}_2(\text{cis-cyclohexane-1,2-diol})_2$ are similar after different initial rates. These data indicate that the same catalytic species is forming after an initial period. $\text{MoO}_2(\text{trans-cyclohexane-1,2-diol})_2$ complex (9) was isolated from the $\text{Mo}(\text{CO})_6$ and $\text{MoO}_2(\text{acac})_2$ catalyzed epoxidation of cyclohexene with $t\text{-BuO}_2\text{H}$ (13). This complex did not form in the absence of hydroperoxide. The same complex was also obtained from the reaction of $\text{MoO}_2(\text{acac})_2$ with epoxycyclohexane and $t\text{-BuO}_2\text{H}$ in benzene or in methylcyclohexane.



When equimolar quantities of hydroperoxide and olefin were used, the epoxidation reaction and hydroperoxide decomposition were competing processes. When 1-octene was used, equal amounts of epoxidation and decomposition products were obtained, whereas with reactive olefins, epoxidation was the main reaction path.

Substitution effects were studied in the $\text{Mo}(\text{naph})$ catalyzed epoxidation of styrene with $t\text{-BuO}_2\text{H}$ by Hiatt (14). The kinetics of the reaction showed that the reaction is first order in hydroperoxide in the range of

0.1-0.41 M, $3/2$ in catalyst at lower concentrations ($0-0.2 \times 10^{-4}$ g-atom of Mo kg^{-1}), $1/2$ at higher concentrations ($0.2-5.5 \times 10^{-1}$ g atom of Mo kg^{-1}), but first order in catalyst when benzene was employed as the solvent.

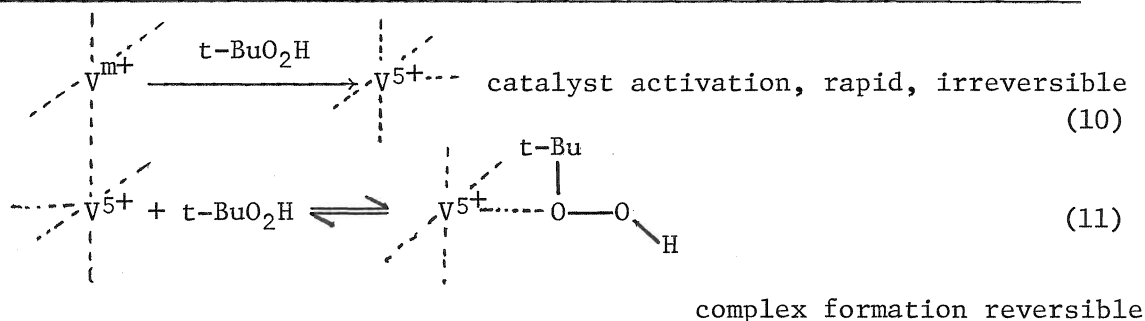
m-Cl, p-Cl, m-Br, p-Br, m-NO₂ and p-Me substituted styrenes were used in the epoxidation, and second order rate constants were determined. The best correlation was obtained with $\log k/k_0$ vs σ ($\rho = -1.37$).

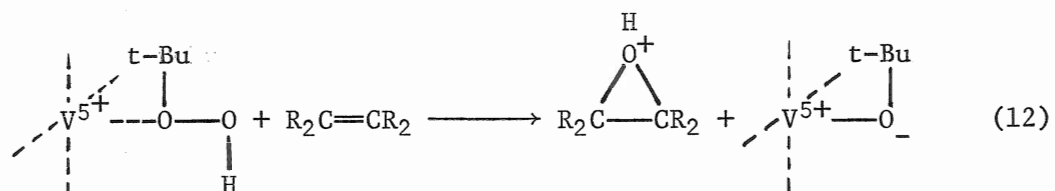
The coproduct alcohol does not inhibit the reaction rate, but catalyst deactivation was observed. This could be due to complexation of the catalyst with further reaction products.

Sapunov et al. (15), in agreement with Gould (11), had shown the formation of molybdenum-olefin, molybdenum-hydroperoxide and molybdenum-olefin-hydroperoxide complexes when molybdenum caproate was used as catalyst, from their kinetic data.

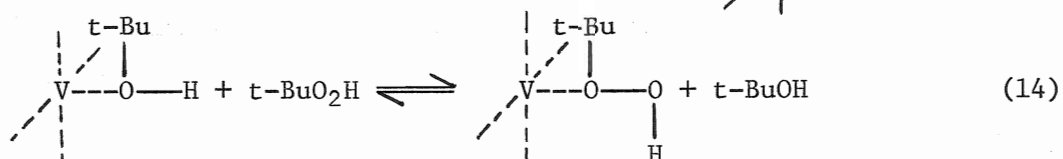
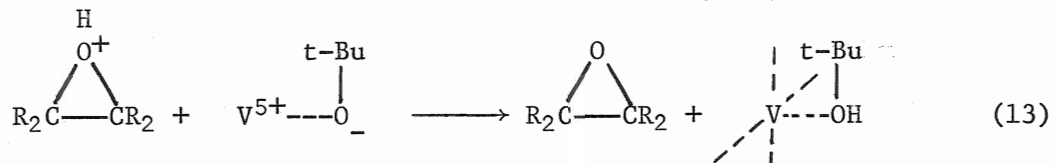
The effect of solvent was also studied by Sapunov et al. (16). Solvents which have good capabilities for complex formation inhibited the reaction quite markedly. In THF and t-butyl acetate, the reaction does not proceed. Also, solvents with high di-electric constants, such as nitrobenzene and dichloroethane, lower the reaction rate.

(a) Mechanism of the epoxidation of olefins in the presence of vanadium catalyst (10)

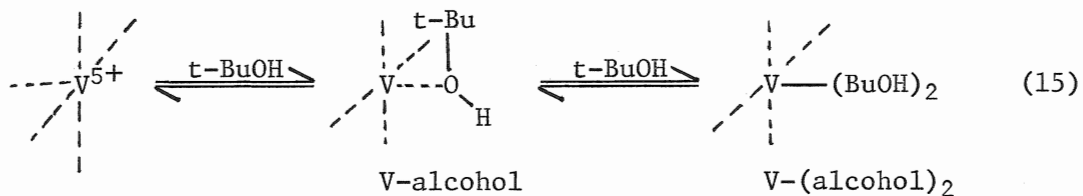




heterolysis, rate determining

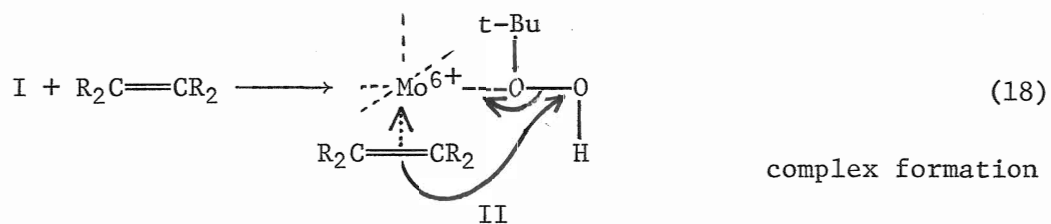
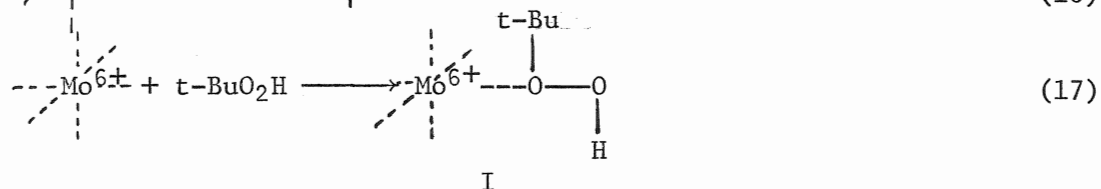


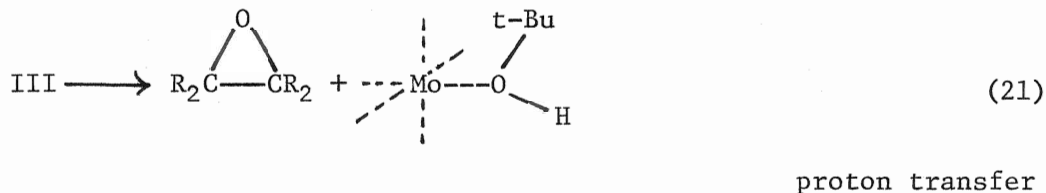
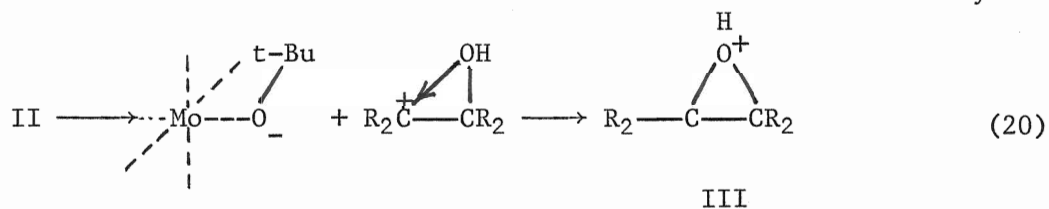
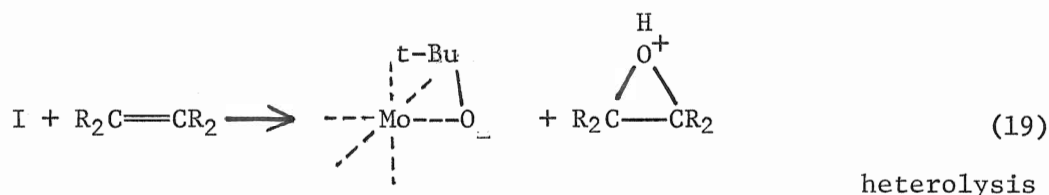
ligand exchange, rapid, reversible



inhibition, reversible

(b) Mechanism of the epoxidation of olefins in the presence of molybdenum catalyst (11)





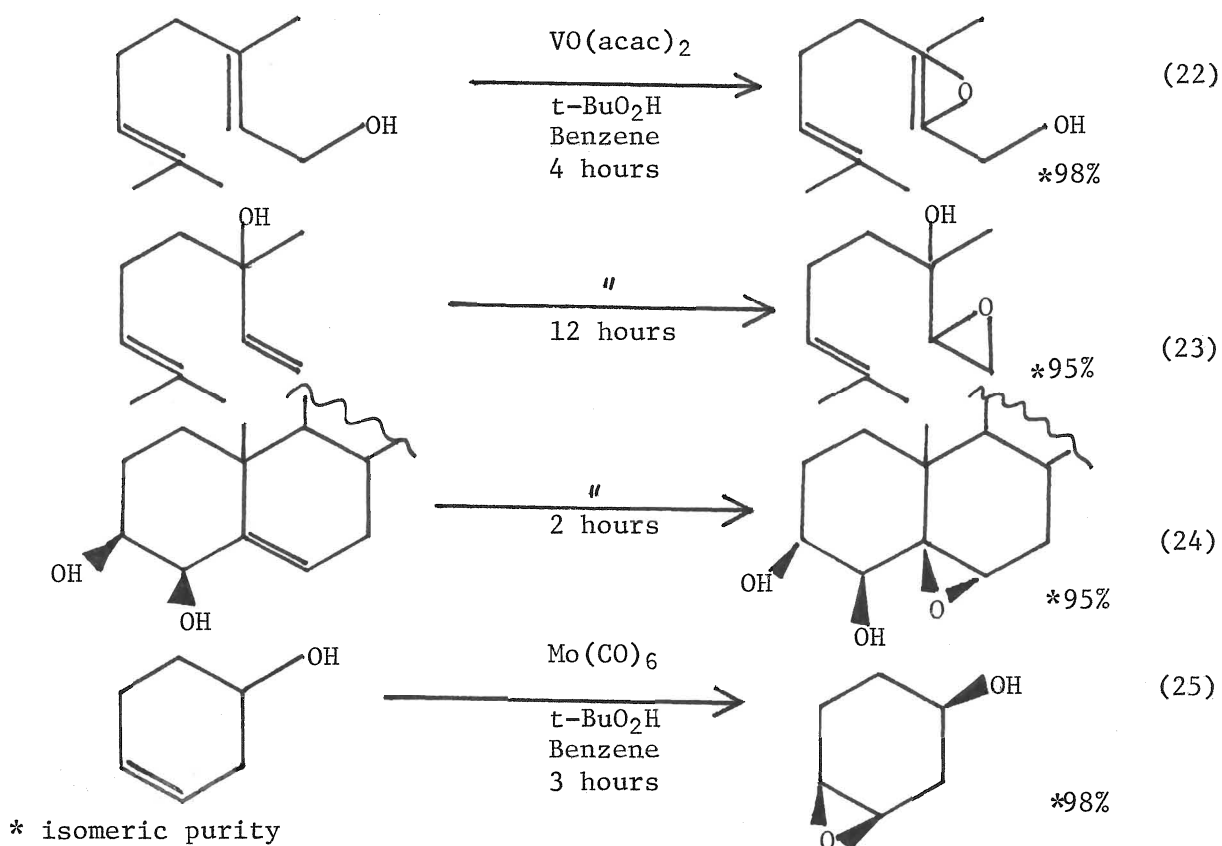
VI. Epoxidation of allyl alcohols in the presence of metal ion

$\text{Mo}(\text{CO})_6$ and $\text{VO}(\text{acac})_2$ have been used as catalysts in the epoxidation of various allyl alcohols with $\text{t-BuO}_2\text{H}$ in a work of Sheng and Zajacek (9). In contrast to olefinic compounds, $\text{VO}(\text{acac})_2$ gave a higher yield of epoxide than did $\text{Mo}(\text{CO})_6$ in the case of allyl alcohols. As noted earlier from the kinetic studies, coproduct alcohol forms complexes with vanadium better than with molybdenum; therefore, the higher activity of vanadium catalyst in the epoxidation of allyl alcohol was explained by the formation of vanadium-allyl alcohol complex.

Farberov *et al.* (29) had shown that the allyl alcohol-vanadium complex caused self-inhibition, and the rate of reaction decreased when the concentration of coproduct alcohol increased.

The stereoselectivity of the metal catalyzed epoxidation of olefinic alcohols was studied by Sharpless and coworkers (30).

The results of the $\text{VO}(\text{acac})_2$ and $\text{Mo}(\text{CO})_6$ catalyzed epoxidation of geraniol, linalol, 4 β -hydroxy-cholesterol and 3-cyclohexene-1-ol with $t\text{-BuO}_2\text{H}$ indicate that the epoxidations are highly selective and yield only one of the possible isomeric epoxy alcohols (Eq. 22-25). The selectivities are much greater in metal-catalyzed systems than in the m -chloroperbenzoic acid system.



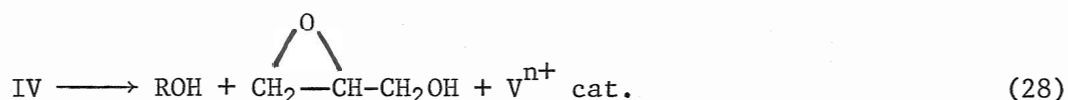
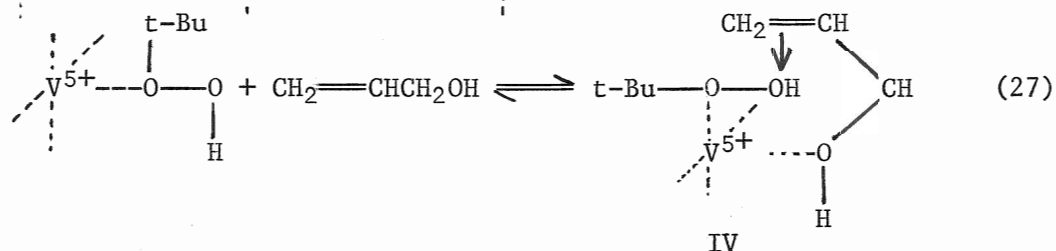
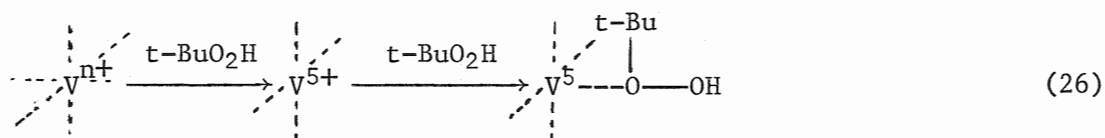
The epoxidation of cyclic homoallyl alcohols is also selective and interesting. The epoxidations of 3-cyclohexene-1-ol and 2-cyclohexene-1-ol showed that homoallyl alcohols reacted faster than allyl alcohols in the $\text{Mo}(\text{CO})_6$ catalyzed system, whereas the epoxidation of allyl alcohols is much faster in the $\text{VO}(\text{acac})_2$ -catalyzed system.

The different stereoselectivity of the epoxidations of acyclic allyl alcohols with $t\text{-BuO}_2\text{H}$, in the presence of $\text{VO}(\text{acac})_2$ and $\text{Mo}(\text{CO})_6$ complexes,

and with *m*-chloroperbenzoic acid were also observed (31-32). It was found that the selectivity of the epoxidation is dependent on the structure of the allyl alcohol and the oxidizing reagent.

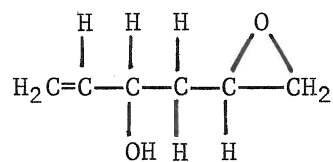
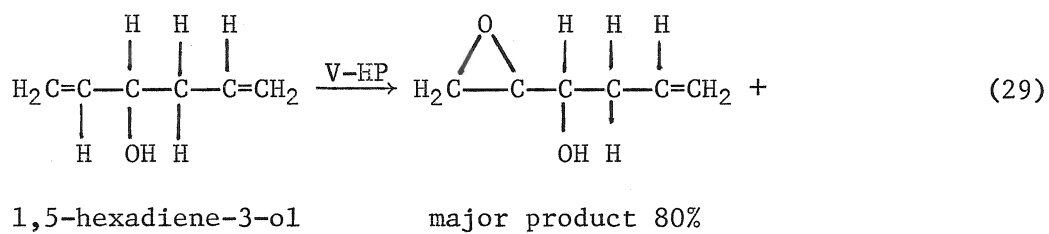
Much work has been done on the epoxidations of allyl alcohols, homo allyl alcohols and bis-homoallyl alcohols; the results are summarized in a recent review article of Sharpless *et al.* (33).

Mechanism of the epoxidation of allyl alcohols

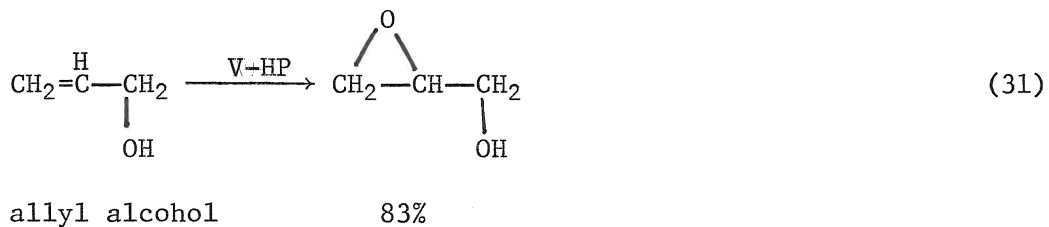
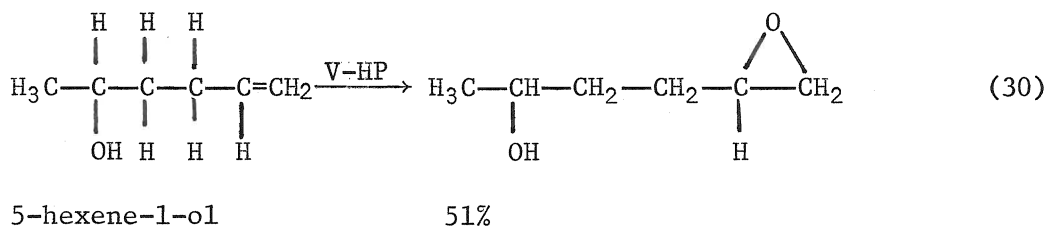


According to the mechanism suggested by Sheng *et al.* (9), after conversion of V^{4+} to V^{5+} , the $\text{t-BuO}_2\text{H-V}^{5+}$ complex forms first; this complex then has to complex with the allyl alcohol (or *vice versa*) before the double bond is epoxidized. This ternary complex is more stable than the hydroperoxide-vanadium complex. The geometry of this complex also makes the epoxidation favorable. Therefore, if the geometry of this complex was changed by the insertion of additional carbon atoms between the double bond and the hydroxyl group, a poor yield of epoxide was obtained. The reaction

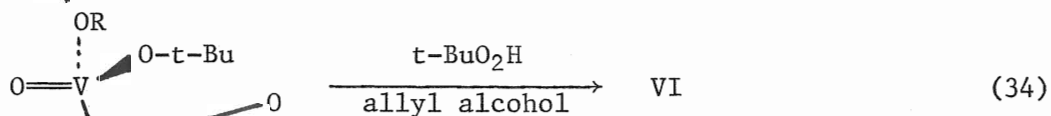
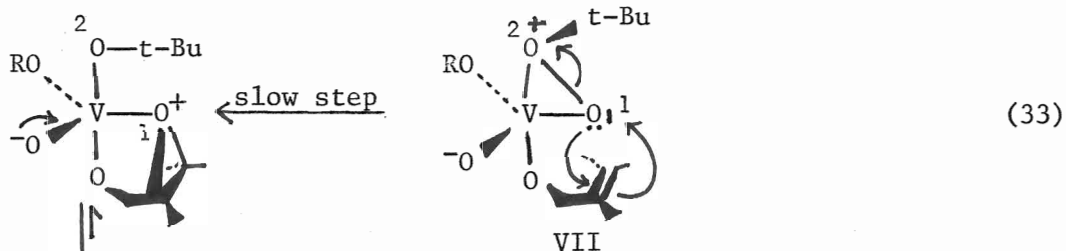
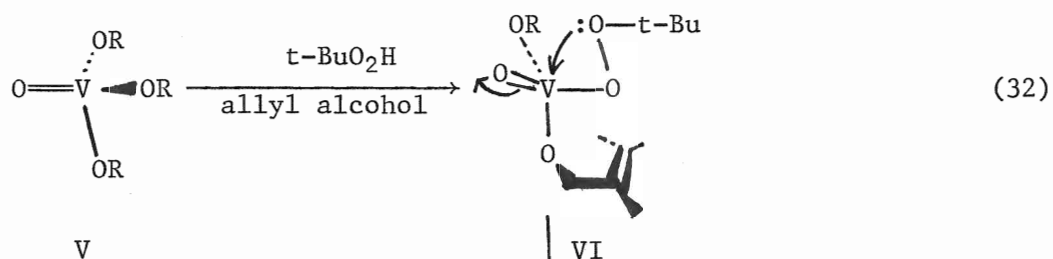
of 1,5-hexadiene-3-ol gave 1,2-epoxide-3-hydroxy-5-hexene as a major product and 5-hexene-2-ol gave a poor yield of the epoxide (9).



minor product 20%



A more detailed mechanism of the epoxidation, which is similar to that suggested by Sheng and Zajacek (9) is given by Sharpless (33). After formation of the V^{5+} alkoxide complexes, the V - t -BuO₂H and allyl alcohol complex forms. The slow step was thought to be the oxygen transfer step. The epoxidation processes involving the attack of olefins on peroxide reagents will be subject to fairly rigid stereoelectronic requirements. In particular, the displacement on the peroxide bond occurs from the back side and along the axis of the O-O bond being broken.



VII. Metal-catalyzed oxidation of phosphines, arsines and stibines

Metal catalyzed oxidation of triphenyl phosphines with $t\text{-BuO}_2\text{H}$ gave reaction rates 10^4 to 10^5 times faster than the H^+ catalyzed reaction (34).

The kinetic data indicate that the oxidation reaction proceeds according to the rate law:

$$\text{Rate} = \frac{-\partial [\text{Ph}_3\text{M}]}{\partial t} = [\text{Ph}_3\text{M}][\text{HP}][k_2 + k_3[\text{cat}]] \quad (36)$$

The oxidation of triphenyl arsine and stibine also follow the same rate law (35). Uncatalyzed and catalyzed reactions proceed together.

There is no effect of catalyst environment in the oxidation of Ph_3P . The catalytic effects of $\text{Mo}(\text{naph})$ and $\text{MoO}_2(\text{acac})_2$ were found to be the same. Also, molybdenum catalysts gave reaction rates 10 times faster than the vanadium catalyst did.

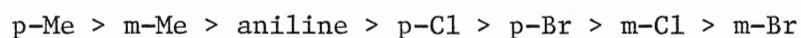
The mechanism of the reaction is similar to that suggested for olefins.

VIII. Metal-catalyzed oxidation of amines and anilines

Various catalysts ($\text{Mo}(\text{CO})_6$, $\text{Mo}(\text{naph})$, $[\text{Mo}(\text{cp})(\text{CO})_3]_2$, $\text{VO}(\text{acac})_2$, $\text{V}(\text{naph})$, $\text{W}(\text{CO})_6$, $\text{Co}(\text{naph})$ and $\text{Co}(\text{acac})_2$) were tested in the oxidation of aniline. Among these complexes, $\text{VO}(\text{acac})_2$ was found to be the most active catalyst. $\text{Mo}(\text{CO})_6$ showed an induction period of 5-10 minutes, during which the catalyst became the active species. $\text{VO}(\text{acac})_2$ -catalyzed oxidation of aniline with $t\text{-BuO}_2\text{H}$ gave nitrobenzene as the product (36). The loss of aniline and the formation of nitrobenzene showed a 1:1 stoichiometry. No reaction occurred in the absence of catalyst. Product analysis showed that no traces of intermediates phenylhydroxylamine, nitrosobenzene were

obtained even though the formation of 1 mole of nitrobenzene requires 3 moles of hydroperoxide.

Substituent effects were studied by a competitive method. The order of reactivity of substituted anilines is given below.



By using σ and σ^+ values versus $\log k/k_0$, good correlations were obtained in both cases with $\rho = -1.42$ and -1.97 . These results indicate an electron deficient transition state.

The rate-determining step is first order in aniline within the range 0.4-2.1 M. Due to autoinhibition of $t\text{-BuOH}$ and catalyst degradation, the order of reaction with respect to catalyst and $t\text{-BuO}_2\text{H}$ could not be determined.

The mechanism of the aniline oxidation is the same as the epoxidation mechanism.

A series of tertiary amines were oxidized with different hydroperoxides to the corresponding oxides in the presence of $\text{Mo}(\text{CO})_6$ and $\text{VO}(\text{acac})_2$ (37). In the $\text{Mo}(\text{CO})_6$ catalyzed oxidation of pyridine with $t\text{-BuO}_2\text{H}$, the rate of reaction was retarded by pyridine-N-oxide after an initial period, due to complexation of pyridine-N-oxide with molybdenum. A white solid which contained 1:2:4 ratio of molybdenum:pyridine-N-oxide:carbon monoxide, precipitated from the reaction solution.

$\text{VO}(\text{acac})_2$ does not catalyze the pyridine oxidation due to strong complexation of vanadium with pyridine-N-oxide.

The greater reactivity of amines compared with olefins is related to the availability of unshared electrons on the nitrogen atom.

IX. Metal-catalyzed oxidation of organic sulfides

Kinetic and mechanistic studies of the metal-catalyzed oxidation of organic sulfides with hydroperoxides were reported by Modena et al. (5,38-45) and Kõseoğlu (46).

$\text{MoO}_2(\text{acac})_2$ and $\text{VO}(\text{acac})_2$ were used as catalysts in the oxidation of di-n-butyl sulfide with t-BuO₂H (5, 38). Kinetic data shows that the reaction order is one with respect to hydroperoxide, sulfide and catalyst within the range of 1×10^{-4} – 2×10^{-3} M for $\text{VO}(\text{acac})_2$ and 0.1×10^{-5} M for $\text{MoO}_2(\text{acac})_2$.

A general rate equation was given as stated below:

$$\text{Rate} = \frac{-\partial [\text{t-BuO}_2\text{H}]}{\partial t} = k_2 [\text{HP}]^m [\text{S}]^n + k_3 [\text{cat}]^p [\text{S}]^q [\text{HP}]^r + k_{\text{dec}} [\text{cat}]^s [\text{HP}]^t \quad (37)$$

When sulfide is in large excess and the ratio of hydroperoxide concentration to catalyst concentration is greater than 8, the uncatalyzed oxidation is much slower and insignificant. Also, the decomposition of hydroperoxide cannot compete with the oxidation reaction; hence, the rate equation becomes

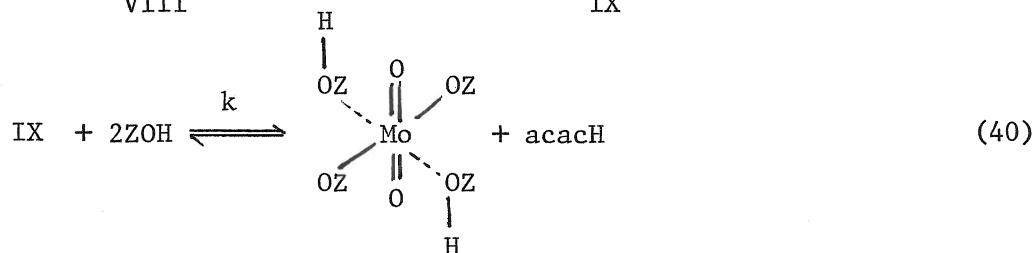
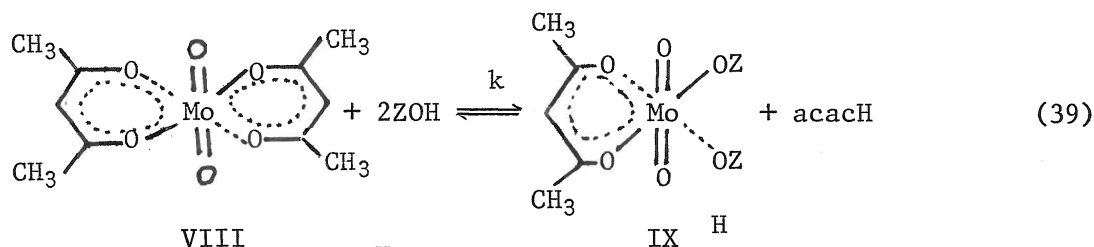
$$\text{Rate} = k_3 [\text{cat}] [\text{S}] [\text{HP}] \quad k_{2\text{obs}} = k_3 [\text{cat}]^p \quad (38)$$

In the oxidation reaction, freshly prepared catalyst solution is required, because the rate constants were found to be 2-20% lower when excess sulfide was added to solutions where a small amount of hydroperoxide had decomposed.

The molybdenum catalyst showed 80 times higher activity than the vanadium catalyst.

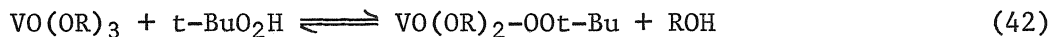
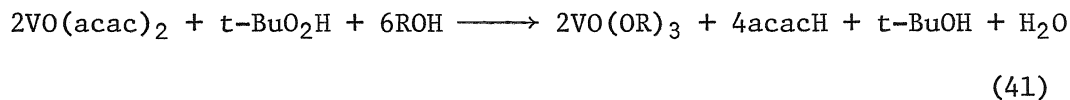
A Hammett plot was obtained from the $\text{VO}(\text{acac})_2$ catalyzed oxidation of p- CH_3 , Cl, H, NO_2 substituted phenylmethyl sulfide with hydrogen peroxide. The ρ value was estimated to be -0.5. This value is small compared to acid catalyzed reaction of arylmethyl sulfides with hydrogen peroxide ($\rho = -1.13$) (47), but the sign of the ρ value is as expected.

The effect of different alcohols (propanol, ethanol and methanol) was studied in the $\text{MoO}_2(\text{acac})_2$ catalyzed oxidation of di-n-butyl sulfide with t-BuO₂H (43). The third order rate constants for isopropanol, ethanol and methanol were found to be 320, 160 and 6 mol⁻² s⁻¹ respectively. The reactivity of these systems gave opposite results to those expected on the basis of alcohol acidity. In the uncatalyzed oxidation, the rate constants, which are opposite to the rate constants of catalytic oxidation are 1, 1.4 and 4 for isopropanol, ethanol and methanol, respectively. Acetylacetone showed retardation of reaction similar to that of CO in the $\text{Mo}(\text{CO})_6$ catalyzed reaction when $\text{MoO}_2(\text{acac})_2$ was employed as the catalyst. The reaction in ethanol containing 2×10^{-3} M of acetylacetone gave a reaction four times faster than the uncatalyzed oxidation; in the absence of acetylacetone, it is 100 times faster. According to results which were obtained in different alcohols and acetylacetone, Modena (43) has shown that $\text{MoO}_2(\text{acac})_2$ is in equilibrium with the solvent alcohol before peroxide containing catalytically active species forms. NMR experiments are also consistent with equilibration.



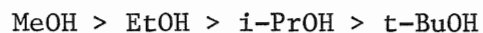
The importance of ligand displacement was shown for catalytic activity of complex. If ligands are tightly held around the metal ion, as in $\text{MoO}_3(\text{dien})$ and $\text{Na}_4[\text{Mo}_2\text{O}_6(\text{EDTA})]$, the complexes are poor catalysts; whereas $\text{MoO}_2(\text{quinolin-8-ol})_2$ and $\text{MoO}_2(\text{acac})_2$ are good catalysts in the epoxidation of cyclohexene by hydroperoxides (48).

Modena had shown that $\text{VO}(\text{OR})_3$ or preferably $\text{VO}(\text{OR})_2\text{OOR}$ are the catalytically active species which form as in Equations 41 and 42 by ligand exchange in the $\text{VO}(\text{acac})_2$ catalyzed oxidation reaction



Their spectroscopic and potentiometric experiments showed that acetylacetonate was completely removed from the coordination sphere of the metal, and in alcoholic solution fast ligand exchange of the V(V) species occurs. An NMR study of ligand exchange of V(V) alkoxides is consistent with the above results (49).

The rates of oxidation of di-n-butyl sulfide with t-BuO₂H, catalyzed by MoO₂(acac)₂ in pure benzene and benzene-ROH mixtures (R = methyl, ethyl, isopropyl or t-butyl) were determined by Modena *et al.* (44). Addition of small amounts of alcohol up to a moderate concentration increased the oxidation rate to a maximum; afterwards rates decreased continuously with increasing alcohol concentration. The degree to which the reaction rate was depressed was observed to depend upon the type of alcohol; the effect of the alcohols tested was in the following order:



This was attributed to

- (i) the capability of alcohols to displace the original ligands (acac),
- (ii) involvement in the transition state,
- (iii) competitive complexation of alcohols with hydroperoxides.

In contrast to Modena and coworkers, Köseoğlu (46) has shown that sulfide plays an important role in the oxidation of sulfides and sulfoxides.

The oxidation of diphenyl sulfide with t-BuO₂H in the presence of Mo(CO)₆ gave diphenyl sulfoxide and diphenylsulfone. The rate equation was expressed by

$$\text{Rate} = k_3[\text{HP}][\text{S}][\text{cat}] + k_3^1[\text{HP}][\text{SO}][\text{cat}] \quad (43)$$

The third order rate constants were found to be 17.2 and 1.55 in ethanol at 35°C for the oxidation of diphenyl sulfide and diphenyl sulfoxide respectively. Diphenyl sulfoxide alone, under the same conditions showed no reactivity. Addition of small amounts of diphenyl sulfide did not change the reactivity. It was concluded that a large amount of diphenyl sulfide is required for the oxidation of diphenyl sulfoxide. Addition of diphenyl

sulfide did not inhibit the reaction. When $\text{VO}(\text{acac})_2$ was used, diphenyl sulfoxide reacted with a rate constant $k_3 = 2.35 \text{ M}^{-2} \text{ s}^{-1}$.

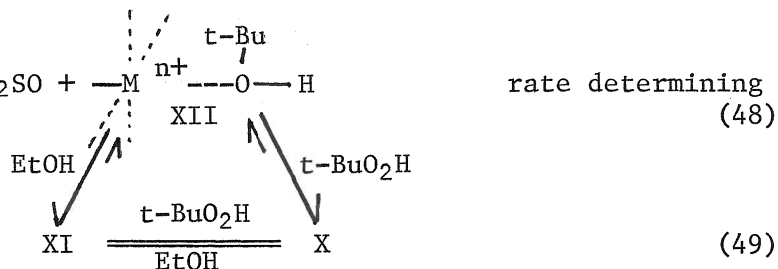
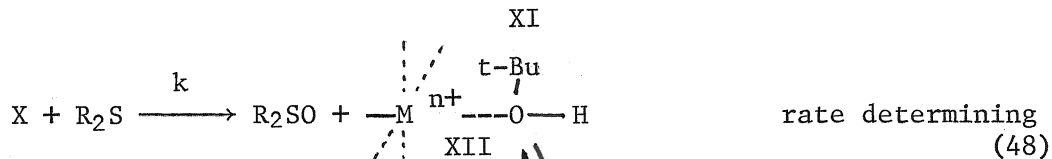
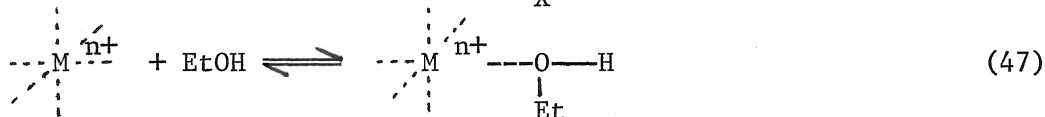
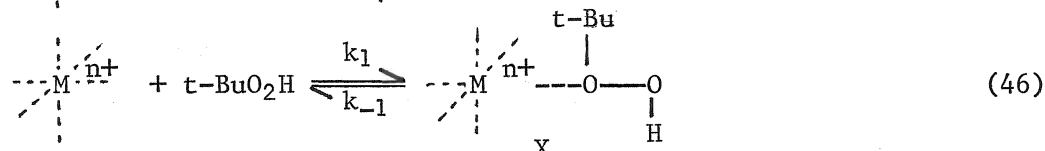
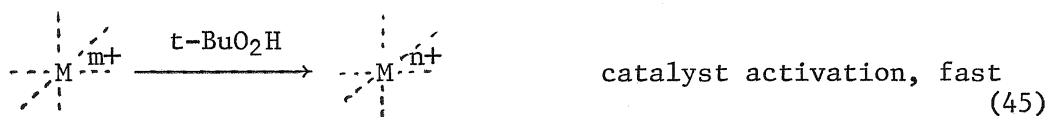
In the oxidation of phenylmethyl sulfide and substituted phenylmethyl sulfide, the following equation gave a good fit.

$$\text{Rate} = k [\text{Mo}(\text{CO})_6][\text{PhSMe}][\text{HP}] \quad (44)$$

The order of reaction with respect to hydroperoxide, sulfide and catalyst in ethanol is first order; this is also true when $\text{Mo}(\text{CO})_6$ in $\text{CHCl}_3/\text{CDCl}_3$ is employed

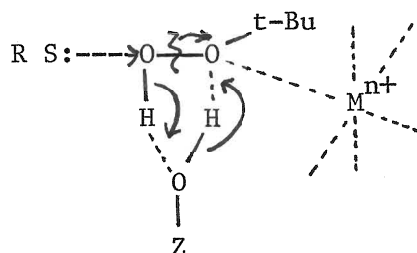
Mechanism of the metal catalyzed sulfide oxidation

For vanadium and molybdenum catalyzed olefin epoxidation and amine oxidation, sulfide oxidation occurs by the nucleophilic attack of the sulfide at the O-O bond of the hydroperoxide-metal ion complex (5).



Coproduct alcohol did not inhibit the reaction in both vanadium and molybdenum catalyzed reactions. This was explained by the efficient regeneration of the active hydroperoxide-metal complex (Eq. 50).

The kinetic first order dependence on sulphide hydroperoxide and vanadium catalyst implies that one molecule of each reactant is involved in the transition state of the rate determining step. The picture of the transition state was drawn by Modena (5); hydrogen transfer was promoted by the intervention of one protic solvent or in its absence by a second molecule of hydroperoxide.



(50)

EXPERIMENTAL

I. Apparatus

IR spectra were recorded on either a Perkin Elmer 225 or a 710B grating infrared spectrometer. ^1H NMR were obtained on a Varian A-60 nuclear magnetic resonance spectrometer with TMS as the internal standard and CDCl_3 as the solvent. GC/Mass spectra were obtained on an AEI MS-30 double beam mass spectrometer which is interfaced to a Pye gas chromatograph. For UV analysis, either a Cary 14 or an Hitachi-Perkin Elmer 124 double beam spectrometer with ethanol as solvent was used. GC analyses were performed on either an F&M 700 laboratory gas chromatograph with thermal conductivity detector or a 5700A Hewlett Packard gas chromatograph with flame ionization detector. Calculations were done using a Wang 2200B calculator. A General Electric 275 W sun lamp was used as a light source.

II. Reagents

(a) The commercially available reagents which were used in this work are listed in Table I. They were used without further purification, except $\text{MoO}_2(\text{acac})_2$, $\text{VO}(\text{acac})_2$, 1-octene and ethanol. Their purification steps were as follows.

$\text{MoO}_2(\text{acac})_2$ was recrystallized by dissolving commercial product in warm acetylacetone. After ligroin was added, the protecting material was filtered off and pure yellow $\text{MoO}_2(\text{acac})_2$ precipitated on standing. The crystals were filtered off, washed with ligroin, dried and kept under nitrogen.

Table 1. Reagents purchased and used.

Chemical	Source	Purity
thioanisole	Aldrich Chemical Company	99%
diphenyl sulfide	" " "	99%+ Gold Label
diphenyl sulfoxide	" " "	97%
diphenyl sulfone	" " "	97%
p-bromothioanisole	" " "	97%
p-chlorothioanisole	Columbia Organic Chemicals	--
p-methylthiophenol	Aldrich Chemical Company	98%
p-methoxyaniline	" " "	97%
p-chloronitrobenzene	" " "	--
4-(methylmercapto)phenol	" " "	--
t-butyl hydroperoxide	" " "	89.09% (checked by titration)
molybdenum hexacarbonyl	ROC/RIC Company	--
molybdenum dioxyacetylacetone	K & K	
vanadium oxyacetylacetone	Alfa Inorganic Inc.	
ethanol (absolute)	commercial	
1-octene	Aldrich Chemical Company	97%
methyl iodide	" " "	99%
p-methylthiobenzaldehyde	Fairfield Chemical Company	--
sodium iodide	BDH Chemicals	99.5%
ethylxanthic acid potassium salt	Eastman Kodak	Technical

Table 1, p. 2

p-hydroxyacetophenone	BDH Chemicals	99%
dimethylthiocarbamoyl chloride	Aldrich Chemical Company	97%
ethylene glycol	J. T. Baker	--
potassium fluoride	Alfa Inorganic Inc.	99%

$\text{VO}(\text{acac})_2$ was recrystallized from acetone.

Absolute ethanol was refluxed with MgO , and distilled. Ethanol was again refluxed with EDTA, and distilled, then kept over 4 Å molecular sieves.

1-Octene was purified by distillation.

(b) The commercially unavailable reagents were synthesized according to the following procedures.

1. Preparation of methyl-p-methylphenyl sulfide

The p-methylthiophenol was methylated according to the adapted procedure of C. M. Suter et al. (50). 100 g (0.813 mole) of p-methylthiophenol and 115 g (excess) of methyl iodide were added to the solution of sodium ethylate which was prepared by dissolving 20 g (0.87 mole) of sodium in 400 mL absolute ethanol. The mixture was refluxed for an hour. After the alcohol was distilled, the residue was poured into water. The oily product was extracted with ether and dried using magnesium sulfate. The crude product was distilled under reduced pressure, producing 86.2 g (0.624 mole) 77% yield of a yellow liquid.

The ^1H NMR spectrum showed signals at $\delta = 2.2$ (3H, singlet), 2.4 (3H, singlet), 7.0 (4H, multiplet). GC/MS analysis showed that the product was pure.

2. Preparation of p-nitrophenylmethyl sulfide

Initially, corresponding thiol was prepared following the method of C. C. Price et al. (51). The alcoholic solution of sodium disulfide which was prepared from 175 g (0.72 mole) of sodium sulfide nanohydrate and

23.4 g (0.729 mole) of sulfur in 95% ethanol was added to the solution of 157.5 g (1 mole) of p-nitrochlorobenzene in 250 mL of boiling ethanol over a period of 15 minutes. Then the solution of 40 g (1 mole) of sodium hydroxide in ethanol was added dropwise within a period of 20 minutes. After boiling the reaction mixture under reflux for 30 minutes, the mixture was cooled and poured into 1 kg of ice and 1500 mL of water. The precipitate was removed by filtration and the filtrate was acidified with concentrated hydrochloric acid until all p-nitrothiophenol precipitated. The yellow precipitate was filtered off and washed with 500 mL water, and then dissolved in 150 mL of 95% ethanol to which 40 g (1 mole) of sodium hydroxide in 1500 mL of water was added. The solution was filtered and p-nitrothiophenol was reprecipitated with concentrated hydrochloric acid from filtrate, and dried in a vacuum dessicator which contained P_2O_5 . The yield of reaction was 51%, m.p. $76^{\circ}C$.

The 1H NMR of the p-nitrothiophenol showed signals at $\delta = 4.0$ (1H, singlet), 7.2-8.4 (4H, multiplet). Also, the identity of product and its purity were checked by GC/MS.

Using the method of C. M. Suter et al. (50), p-nitrothiophenol was methylated to p-nitrophenylmethyl sulfide. 70 g (0.45 mole) of p-nitrothiophenol and 70 g (excess) of methyl iodide were added to the solution of sodium ethylate made by dissolving 12 g (0.52 mole) of sodium in 225 mL of absolute ethanol, and the mixture was refluxed for two hours. The ethanol was removed by distillation, and the reaction mixture poured into water. The crude product was extracted with ether, dried using sodium sulfate and ether was evaporated in steam bath. 60 g (78.8 % yield) of the pure

p-nitrophenylmethyl sulfide was obtained after recrystallizing the crude product from methanol.

The p-nitrophenylmethyl sulfide was further identified by ^1H NMR and GC/MS analysis. The ^1H NMR spectrum of the p-nitrophenylmethyl sulfide showed signals at $\delta = 2.5$ (3H, singlet), 7.1-8.2 (4H, multiplet). According to GC/MS analysis, the compound is pure.

3. Preparation of p-methoxyphenylmethyl sulfide

Initially, p-methoxyphenylmethyl sulfide was prepared following the method of C. M. Suter et al. (50). To a solution of 300 g (1.875 mole) of potassium ethyl xanthate in 700 mL of water, the cold solution of 120 g (1 mole) of diazotized p-methoxyaniline, in which the free acid was neutralized by the addition of sodium acetate, was added slowly at 70-80°C. The reaction mixture was refluxed and stirred for an hour. Then the mixture was cooled and the oil was extracted with ether. This oily material was then refluxed for three hours with a solution of 115 g of potassium hydroxide in 2 L of 95% ethanol containing 20 g of glucose. After the distillation of ethanol until the mixture volume was about 300 mL, the mixture was acidified with cold dilute sulfuric acid, and 2 g of zinc dust was added. The crude product was removed by steam distillation, extracted with ether and dried over calcium chloride. Finally, the p-methoxythiophenol was distilled under reduced pressure (108°C, 18 mm). The yield was 27.7 g (19.78%).

The ^1H NMR spectrum showed signals at $\delta = 3.3$ (1H, singlet), 3.6 (3H, singlet), 6.7-7.4 (4H, multiplet). The purity of the product was checked by GC/MS.

p-Methoxythiophenol was methylated to produce the p-methoxyphenylmethyl sulfide by using the method of the same author (50). Starting from 18 g (0.128 mole) of p-methoxythiophenol, 17 g (excess) of methyl iodide and the solution of sodium ethylate, 15.5 g (78%) of pure p-methoxyphenylmethyl sulfide was obtained.

The ^1H NMR analysis showed peaks at $\delta = 2.3$ (3H, singlet), 3.6 (3H, singlet), 6.6-7.4 (4H, multiplet). GC/MS analysis showed that p-methoxyphenylmethyl sulfide was pure.

4. A simpler way of preparing p-methoxyphenylmethyl sulfide

In the above synthesis, the yield of the title compound was low compared to the given value by C. M. Suter *et al.* (50). Therefore, the methylation of commercially available 4-(methylmercapto)phenol was found to be easy and efficient way. The methylation reaction was followed with the same procedure given by C. M. Suter *et al.* (50). Starting from 75 g (0.535 mole) of 4-(methylmercapto)phenol, 76.6 g (excess) of methyl iodide and the solution of sodium ethylate (13 g (0.595 mole) of sodium in 300 mL absolute ethanol), 61 g (74%) of p-methoxyphenylmethyl sulfide was obtained. The identity and purity of the sample were checked by ^1H NMR, GC/MS and UV analysis.

The ^1H NMR spectrum showed peaks at $\delta = 2.3$ (3H, singlet), 3.6 (3H, singlet), 6.6-7.4 (4H, multiplet). UV spectrum showed maximum at 258.4 nm (lit. value (52) 256 nm).

5. Preparation of p-acetylphenylmethyl sulfide

p-Acetylphenylmethyl sulfide was prepared from the corresponding thiophenol, which was prepared from p-hydroxyacetophenone by the method of Newman and Karnes (53).

46 g (0.338 mole) of p-hydroxyacetophenone was dissolved in 215 mL of water containing 19 g (0.338 mol) of potassium hydroxide. The solution was cooled below 10°C in a 500 mL three-necked flask. A solution of 51.5 g (0.42 mol) of dimethylthiocarbamyl chloride in dry dimethyl formamide was added over 30 minutes to the stirred solution; during this period the temperature did not exceed 12°C. After the addition was complete, the solution was warmed to room temperature. The reaction mixture was then made alkaline by the addition of 100 mL of 10% potassium hydroxide solution and was shaken three times with 100 mL portions of (dry purified) benzene. The organic layer was collected, washed with a saturated solution of sodium chloride, and dried with anhydrous sodium sulfate. 47.5 g (0.213 mole; 64% yield) of 4-acetophenylthiocarbamate was obtained after distillation of the solvent.

The ^1H NMR spectrum showed signals at $\delta = 2.60$ (3H, singlet), 3.35 (3H, singlet), 3.4 (3H, singlet), , 7-8 (4H, multiplet).

According to Carter (54), a protecting group is necessary for the carbonyl group because of its reactivity in the pyrolysis reaction. The protecting group was therefore added to the p-acetophenylthiocarbamate by the following standard method (55): 46.5 g (0.21 mole) of thiocarbamate, 14 mL (0.214 mole) of ethylene glycol, 0.0613 g p-toluene sulfonic acid and 75 mL of benzene were refluxed in a 500 mL round-bottom flask (equipped with a water separator and condenser with drying tube) until 4 mL of water was collected in the separator trap. The reaction mixture was then washed with 25 mL of 10% sodium hydroperoxide solution, five 20 mL portions of water, and dried with anhydrous magnesium sulfate. The benzene was removed to yield the crude product, which was recrystallized from methanol (yield 21.9 g, 0.084 mole, 40%).

The ^1H NMR spectrum of the ketal showed signals at $\delta = 1.60$ (3H, singlet), 3.3 (3H, singlet), 3.5 (3H, singlet), 3.75-4.05 (4H, multiplet), 7.0-6.7 (4H, multiplet).

The pyrolysis of the thiocarbamate was accomplished in a sand bath at 220°C over two hours. A solution of 12 g (0.214 mole) of potassium hydroxide in 20 mL of water and 140 mL of ethylene glycol was then added to the flask. After cooling, the mixture was refluxed for 2.5 hours. The cooled reaction mixture was then poured on to 300 g of ice. After the ice had melted, the mixture was shaken twice with 200 mL portions of chloroform. The organic layers were combined, dried over magnesium sulfate, and distilled. 15.4 g (0.101 mole) of 4-thioacetophenone was obtained.

The ^1H NMR spectrum showed signals at $\delta = 2.50$ (3H, singlet), 3.75 (1H, singlet), 7.1-7.9 (4H, multiplet).

The method of C. M. Suter (50) could not be used in the methylation of 4-thioacetophenone, because of the condensation reaction which occurs in the presence of base; therefore, the procedure of Clark and Miller (56) was followed. 14.4 g (0.0947 mole) of 4-thioacetophenone, 7.511 g (0.13 mole) of potassium fluoride and 13 mL (excess) of iodomethane were refluxed in 60 mL of dry DMF for three hours. The mixture was then cooled to room temperature, shaken three times with diethyl ether, and the combined organic layers were washed with water to remove DMF. The ether layer was dried over anhydrous magnesium sulfate, and the solvent distilled. After recrystallization of the crude product, 6.64 g (0.04 mole, 42% yield) of p-acetylphenylmethyl sulfide was obtained.

The ^1H NMR spectrum showed signals at $\delta = 2.5$ (3H, singlet), 2.60 (3H, singlet), 7.2–8.0 (4H, multiplet). GC/MS analysis showed that p-acetylphenylmethyl sulfide was sufficiently pure.

6. Preparation of phenylmethyl sulfoxide

The synthesis of phenylmethyl sulfoxide was accomplished by the method of C. R. Johnson (57). 3 g (0.024 mole) of phenylmethyl sulfide was added to the solution of 5.25 g (0.025 mole) of sodium metaperiodate in water. Enough methanol was added until the phenylmethyl sulfide dissolved. The mixture was stirred and kept in an ice bath overnight (approximately 12 hours). After removal of precipitated sodium iodate by filtration, the filtrate was extracted with chloroform. The extract was dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator. The pure sulfoxide was distilled under reduced pressure (18 mm Hg, 117°C). 2.5 g (0.0178 mole) 74% of phenylmethyl sulfoxide was isolated. The identity and purity were checked by ^1H NMR and GC/MS analysis.

The ^1H NMR spectrum showed signals at $\delta = 2.7$ (3H, singlet), 7.4–7.85 (5H, multiplet).

III. Kinetic Studies

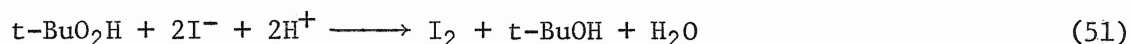
(a) Oxidation of organic sulfides

Previously (46), it was found that premixing and preequilibration of solutions give reproducible reactions. Therefore the same procedure was followed.

The catalyst was dissolved in ethanol in a 25 mL volumetric flask and 500 μ L of catalyst solution was added to the sulfide solution in a 10 mL volumetric flask which was then filled with ethanol. The solution of t-BuO₂H was prepared in a 10 mL volumetric flask. Both solutions then were pre-equilibrated for an hour at reaction temperature. Also for reactions under UV light, both solutions were irradiated before reaction. Reactions were accomplished under either argon or nitrogen atmosphere. Aliquots were taken at different time periods. The disappearance of t-BuO₂H was determined by iodometric titration. Also, attempts were made to determine the disappearance of sulfide and the formation of sulfoxide by gas chromatography.

1. Titrations

Iodine which was produced from the oxidation of iodide ion by t-BuO₂H (eq.51) was titrated with sodium thiosulfate solution to produce iodide ion (eq.52).



500 μ L of the sample and enough sodium iodide were added to 20/80 acetic acid/isopropanol solution and refluxed for four minutes then titrated.

2. Gas chromatographic analysis

An F&M 700 gas chromatograph which has a thermocouple detector was used with a $\frac{1}{4}$ inch x 6 feet copper column packed with 3% silicone rubber gum (SE-30) on Chromosorb W 80/100 mesh. Helium was used as the carrier gas. The calibration curves were prepared for phenylmethyl sulfide and phenylmethyl sulfoxide in ethanol which was used as an internal standard.

5 μ l of sample was injected. GC conditions were

oven = 160°C to 5°C/min until 280°C

injection port = 295°C

detector = 300°C

helium flow = 150 mL/min.

S. S. Köseoglu (46) showed that it is not possible to analyze sulfide and sulfoxide in the presence of $t\text{-BuO}_2\text{H}$ by gas chromatography. It is due to the reaction between unreacted sulfide and $t\text{-BuO}_2\text{H}$ in the injection port. $(\text{EtO})_3\text{P}$ was used to reduce the unreacted $t\text{-BuO}_2\text{H}$ to $t\text{-BuOH}$ before injection. But E. Amonoo-Neizer et al. (58) showed that dimethyl sulfoxide oxidises phosphites to phosphates, forming dimethyl sulfide. Similar to this work, diphenyl sulfoxide and triethylphosphite were mixed at room temperature. 5 μ L of sample was injected into the gas chromatograph. Results showed that diphenyl sulfide was formed as a product (App. 1). Therefore, gas chromatography could not be used to follow sulfide to sulfoxide conversion. It was used, however, to determine end-products after all of the $t\text{-BuO}_2\text{H}$ was consumed.

(b) Competition reactions

The difference in these reactions was that two different sulfides were oxidized together in the same media.

1. Gas chromatographic studies

The F&M 700 Laboratory gas chromatograph was used with a $\frac{1}{4}$ inch x 6 feet copper column packed with 5%FFAP on Chromosorb G. The calibration curves were prepared for each sulfide in ethanol. The products and their concentrations were analyzed at the end of reaction. GC conditions for Run 141 were

oven = 175°C, 20°C/min to 250°C

detector = 310°C

injection port = 250°C

helium flow = 143 mL/min.

GC conditions for runs 132, 142 were

oven 175°C, 5°C/min to 200°C

20°C/min to 250°C

detector = 310°C

injection port = 300°C

helium flow = 150 mL/min.

Under the above conditions, good separation was observed in each case. The chromatographs for runs, 141 and 132 are in Appendix 2.

2. UV spectral analysis

The results obtained from gas chromatographic analysis are not able to show relative reaction rates. Therefore, analyses were performed using

an UV spectrophotometer. Extinction coefficients of phenylmethyl sulfide, phenylmethyl sulfoxide, p-methoxyphenylmethyl sulfide, p-methoxyphenylmethyl sulfoxide, p-nitrophenylmethyl sulfide and p-nitrophenylmethyl sulfoxide were determined at their maxima which are 254, 237, 257, 243, 340, 284 nm respectively. Concentrations were calculated according to the Beer Lambert Law. The equations are shown and the extinction coefficients are listed in Appendix 3.

For analysis, 10 μ L of a sample was added to 50 mL volumetric flask with Eppendorf multi volume tip ejecting micropipet. The flask was then filled to the mark with ethanol.

(c) Oxidation of 1-octene

25 mL of catalysis solution in benzene and 28 mL of octene plus 15 mL of t-BuO₂H in benzene were pre-equilibrated at 85°C for an hour then mixed. Reaction temperatures were observed by inserting a thermometer in the reaction solution. Changes of $\pm 1^\circ\text{C}$ were observed due to temperature changes of the constant temperature bath at high temperatures. Reactions were done in an air atmosphere.

The disappearance of t-BuO₂H was analyzed by iodometric titration, and the formation of 1-epoxyoctane was followed by gas chromatography. GC conditions were

oven = 50°C , 20°C/min to 300°C

injection port = 200°C

detector = 300°C

helium flow = 150 mL/min

Since the reaction was run at 85°C, the influence of injection port temperature to reaction was negligible.

(d) Preparation of IR samples

Mo(CO)_6 was irradiated in cyclohexane, 1-octene and benzene separately in nitrogen atmosphere at different time periods. Spectra were performed in 0.2 mm thick KBr cells on a Perkin Elmer 225 grating infrared spectrometer.

RESULTS AND DISCUSSION

These are presented under two main headings: 1. The Effect of Light Intensity on the Rate of Reactions Catalyzed by Molybdenum Compounds, and 2. Substituent and Solvent Effects on the Molybdenum-Catalyzed Reaction of Hydroperoxides with Organic Sulfides.

Under Light Intensity Effects, both oxidation of sulfides and epoxidation of olefins are considered. A section on co-oxidation of sulfides and olefins is included, as seeming to fit best here although irradiation effects were not measured.

The reactions measuring substituent and solvent effects were carried out under "normal laboratory lighting" although effects of lighting level were known. The justification for this is that reactions catalyzed using $\text{MoO}_2(\text{acac})_2$ could be accelerated only by very high light intensity. The results are thus comparable to those of Modena et al. (38), who are apparently ignorant of illumination effects.

I. The effect of light on reactions

The oxidation of diphenyl sulfide was accomplished by $t\text{-BuO}_2\text{H}$ in the presence of Mo(CO)_6 in ethanol at 35°C . Table 2 lists the third order rate constants and the reaction conditions. Although the reactions were performed under the same conditions, the rate constants differed (Runs 11-15). However, straight forward reactions which are consistent with each other were observed in Runs 16 and 17. The only difference between those reactions was the preparation of the catalyst solution. The irreproducible results were obtained when the catalyst solution was prepared in a large volume (500 mL) and accidentally exposed to daylight during its preparation. In Runs 16 and 17, the small amount of catalyst solution (50 mL) was prepared in the lab without any exposure to daylight. The effect of light could not be determined at that time; the only influencing factor was thought to be the large volume of catalyst solution and the catalyst itself. This factor was ruled out when $\text{MoO}_2(\text{acac})_2$ was employed as catalyst (see Table 7 in the next section). The question behind the activity of Mo(CO)_6 was unanswered and left for the time being.

As mentioned previously, Köseoğlu had shown that sulfide played an important role in the catalyst activation, i.e., that sulfide had an influence on the structure of the catalyst. The work was therefore continued in order to synthesize such a complex between sulfides or sulfoxides with Mo(CO)_6 .

Table 2. $\text{Mo}(\text{CO})_6$ -catalyzed oxidation of diphenyl sulfide with $t\text{-BuO}_2\text{H}$ in ethanol.^a

Run Number	$[\text{Ph}_2\text{S}]$	$[t\text{-BuO}_2\text{H}]$	$[\text{Mo}(\text{CO})_6] \times 10^5$	$k_3^b \text{ M}^{-2} \text{ min}^{-1}$	$k_3^c \text{ M}^{-2} \text{ min}^{-1}$
11	0.406	0.800	100.21	8.59	--
12	0.406	0.799	100.03	6.13	--
13	0.406	0.799	100.20	11.94	--
14	0.406	0.799	100.20	15.15	--
15	0.406	0.799	100.42	6.30	--
16	0.408	0.799	98.10	9.83	8.91
17	0.406	0.800	93.56	9.83	8.26

^a at 35°C in nitrogen atmosphere

^b obtained from titrations and CSEFA/SEMIH program was used (Ref. 46).

^c obtained from UV analysis and titrations/ CSEFA/SEMIH2 program was used for calculation (Ref. 46).

Syntheses of sulfide + Mo(CO)_6 , Cr(CO)_6 , W(CO)_6 complexes and sulfoxide + Mo(CO)_6 , Cr(CO)_6 , W(CO)_6 complexes were attempted by W. Strohmeier et al. (59) using thiophene, dimethyl sulfoxide, thiophene oxide, diphenyl sulfoxide, ethylene sulfide and sulfur dioxide. Complexes of W(CO)_6 , Cr(CO)_6 with sulfides and sulfoxides, and $\text{Mo(CO)}_5\cdot\text{S(CH}_2)_4$, $\text{Mo(CO)}_5\cdot\text{SO(CH}_3)_2$ and $\text{Mo(CO)}_5\text{SO(CH}_2)_4$ were obtained, but $\text{Mo(CO)}_5\text{Ph}_2\text{SO}$ and $\text{Mo(CO)}_5\text{SO(OCH}_2)_2$ complexes could not be obtained. They concluded that light had an influence on the formation of these sulfide and sulfoxide complexes with metal hexacarbonyls.

In order to study this idea further, an attempt was made to observe the physical changes of the solutions of Mo(CO)_6 plus Ph_2S in ethanol and Mo(CO)_6 plus Ph_2SO in ethanol in the dark and under the normal lab light conditions. Under normal light conditions, the colour of Mo(CO)_6 plus Ph_2SO solution changed from light yellow to blue in two days, whereas the colour changes took a week to occur in the dark. Similarly, the colour of Mo(CO)_6 plus Ph_2S changed from light yellow to dark green in two weeks under normal light conditions; this same change required a month in the dark. However, no $(\text{Ph}_2\text{SO})_x\text{Mo(CO)}_{6-x}$ and $(\text{Ph}_2\text{S})_x\text{Mo(CO)}_{6-x}$ complexes were obtained. These colour changes were due to the formation of new complexes. Therefore, attention was turned to kinetic reactions which would be done under dark and light conditions.

Reactions were carried out using phenylmethyl sulfide as a nucleophilic substrate, $t\text{-BuO}_2\text{H}$ as an oxidant, and Mo(CO)_6 , or $\text{MoO}_2(\text{acac})_2$ as catalysts at 35°C in nitrogen atmosphere. The results are summarized in Table 3;

Table 3. The oxidation of phenylmethyl sulfide by t-BuO₂H in the presence of either Mo(CO)₆ or MoO₂(acac)₂, under various light conditions, in ethanol.^a

Run Number	[PhSMe]	[t-BuO ₂ H]	Catalyst	[cat] x 10 ⁵	Light conditions	T°C	k ₂ x 10 ² M ⁻¹ min ⁻¹	k ₃ M ⁻² min ⁻¹
93	1.009	0.202	MoO ₂ (acac) ₂	2.503	dark	35	0.655	261.0
53	1.005	0.206	MoO ₂ (acac) ₂	2.407	normal	35	5.49	2279
95	1.014	0.204	MoO ₂ (acac) ₂	2.668	150 W spot light	35	8.31	3114
96	1.007	0.207	MoO ₂ (acac) ₂	2.667	275 W UV light	35	10.2	3843
151	1.023	0.209	MoO ₂ (acac) ₂	2.533	UV	30	6.17	2437
152	1.022	0.206	MoO ₂ (acac) ₂	2.533	UV	25	3.79	1496
97	1.008	0.204	--	--	UV	35	no reaction	
157	1.020	0.205	Mo(CO) ₆	2.821	UV	35	10.11	3582
125	1.021	0.206	Mo(CO) ₆	2.765	normal	35	0.0357	12.90
153	1.022	0.211	Mo(CO) ₆	2.897	UV	31	7.84	2707
156	1.020	0.211	Mo(CO) ₆	2.821	UV	19	3.17	1125
154	1.020	0.209	Mo(CO) ₆	2.727	UV	25	5.26	1928
158	1.023	0.206	Mo(CO) ₆	2.814	UV	39	2.87	4576

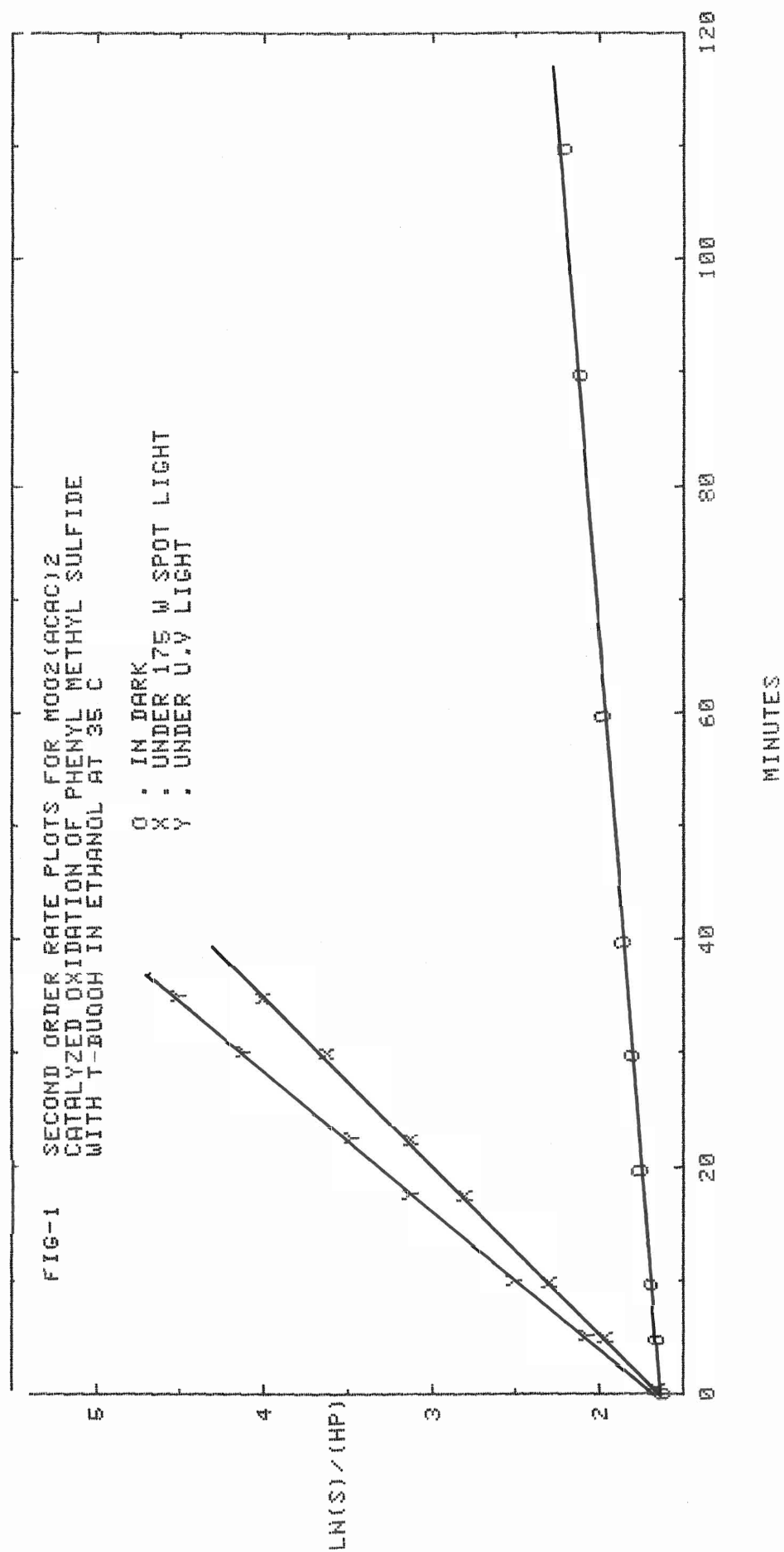
^a under nitrogen atmosphere

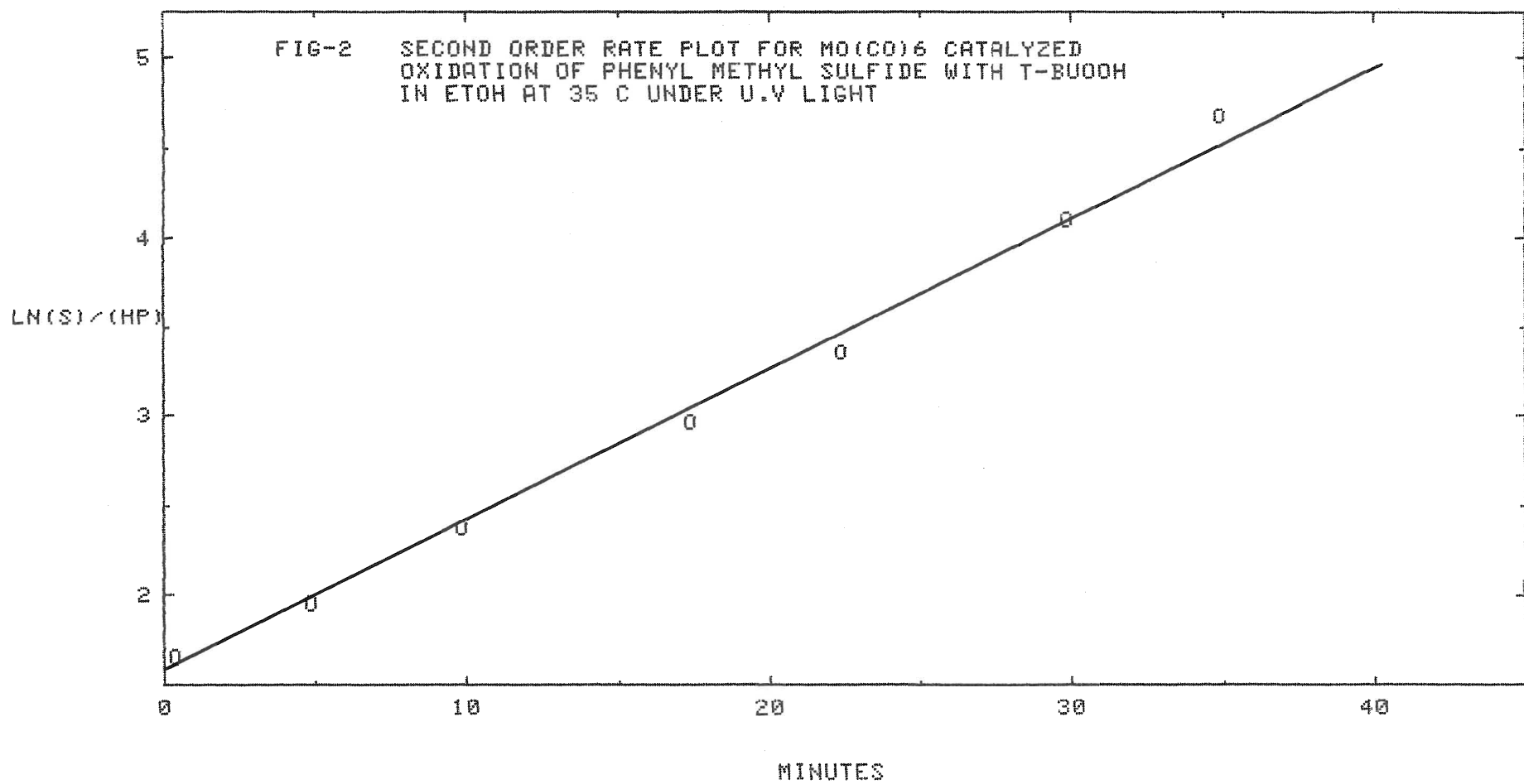
the oxidations follow second order kinetics under all conditions (Figs. 1 and 2) except $\text{Mo}(\text{CO})_6$ -catalyzed phenylmethyl sulfide oxidation under normal light conditions at 35°C . This reaction showed reproducibility and an increase in rate with time (Fig. 3). An approximate rate was calculated using the first four points from the second order rate plot. No decomposition of $t\text{-BuO}_2\text{H}$ in the presence of catalyst and no uncatalyzed oxidation of phenylmethyl sulfide was observed at 35°C under UV radiation in 35 minutes.

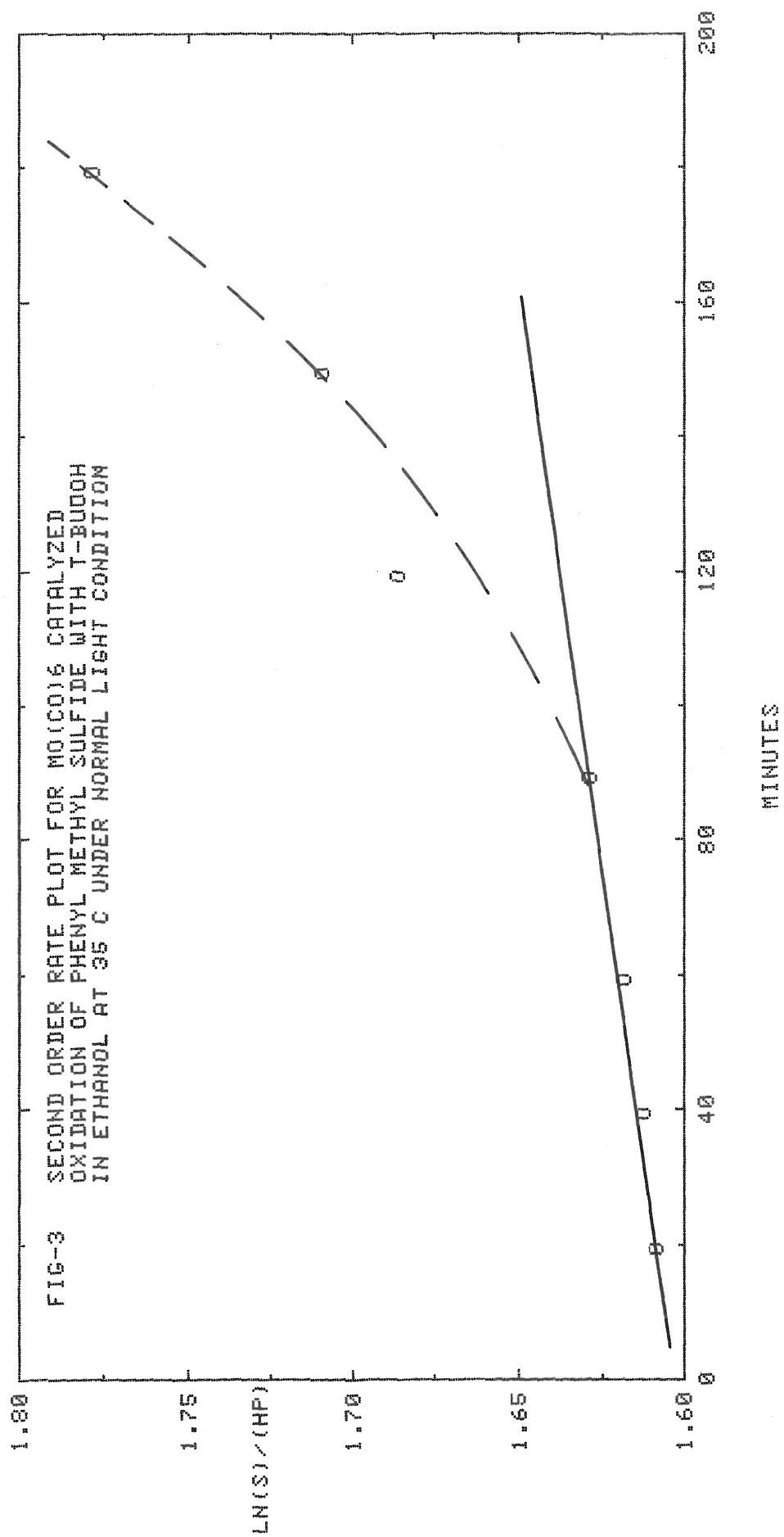
As is clearly seen from Table 3, the rate constants increase when the lighting conditions of the reaction environment change from dark to light. The UV light increased the oxidation rate to 1.7 times greater than that found under normal light conditions in $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation, whereas in $\text{Mo}(\text{CO})_6$ -catalyzed oxidation reaction proceeded 278 times faster under UV light than under normal light. No $\text{Mo}(\text{CO})_6$ -catalyzed oxidation reaction was done in the dark because it was not needed, and sufficient information was obtained. Interpretation of the results of either $\text{Mo}(\text{CO})_6$ - or $\text{MoO}_2(\text{acac})_2$ catalyzed phenylmethyl sulfide oxidation with $t\text{-BuO}_2\text{H}$ under different light conditions involves a number of general considerations:

- (i) the formation of catalytically active molybdenum(VI) species,
- (ii) the complexation of sulfides, alcohols and $t\text{-BuO}_2\text{H}$ with the catalyst,
- (iii) the effect of light on the nucleophilicity of sulfide.

The difference between the activity of $\text{Mo}(\text{CO})_6$ and $\text{MoO}_2(\text{acac})_2$ can be explained by the formation of catalytically active molybdenum(VI) species.

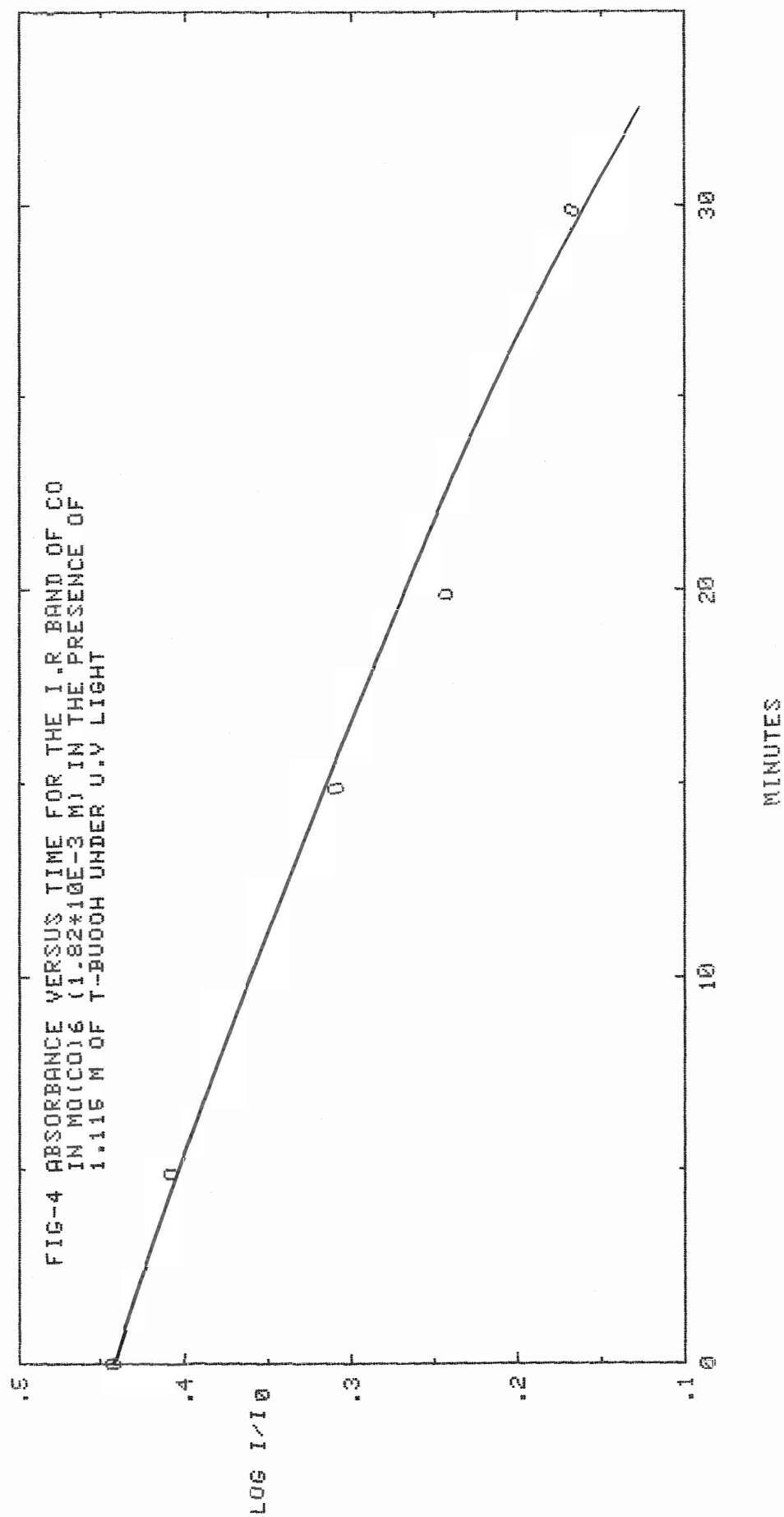






Kinetic reactions, in this work, indicate that molybdenum(0) in Mo(CO)_6 is partially converted to the molybdenum(VI) oxidation state with $t\text{-BuO}_2\text{H}$ at 35°C . As seen from Figure 3, the rate of reaction increases with time. This clearly shows that oxidation of molybdenum(0) to molybdenum(VI) occurs slowly. When the reaction was run under UV radiation, $t\text{-BuO}_2\text{H}$ and UV radiation together cause the rapid conversion of molybdenum(0) to molybdenum(VI).

The oxidation of Mo(0) to molybdenum(VI) occurs by removing six d electrons from the metal ion. If these six electrons are removed, the structure of Mo(CO)_6 is expected to change because of the poor donating and good π acceptor ability of $\text{C}\equiv\text{O}$ ligand. By removing six d electrons, molybdenum becomes a strong Lewis acid; in the presence of strong Lewis bases (compared to carbon monoxide) such as R_2S , ROH and $t\text{-BuO}_2\text{H}$, the formation of molybdenum hydroperoxide, sulfide and alcohol complexes is expected. No CO ligand is expected to be around the molybdenum, so the stretching frequency of the CO group should disappear in the IR spectrum of Mo(CO)_6 . Experiments were done, therefore, to observe the CO band. The IR spectrum of Mo(CO)_6 consists of one band at 1980 cm^{-1} in ethanol (Appendix 4). This band disappears slowly in the presence of $t\text{-BuO}_2\text{H}$ under UV radiation in 30 minutes (Fig. 4, Appendix 5) when the molar ratio of $t\text{-BuO}_2\text{H}$ to Mo(CO)_6 is 612/1. This ratio is very small compared to the ratio in the kinetic reactions (8000/1). If the $t\text{-BuO}_2\text{H}/\text{Mo(CO)}_6$ molar



ratio of 8000/1 is used in IR experiments, a rapid decrease of the intensity of $C\equiv O$ band should be observed. Since $Mo(CO)_6$ has very low absorption below 1.82×10^{-3} M, the $t-BuO_2H/Mo(CO)_6$ molar ratio of 8000/1 in ethanol could not be prepared, because $Mo(CO)_6$ has to be dissolved in concentrated $t-BuO_2H$. This was dangerous work which caused a fire and an explosion.

The same rapid conversion was also reported at high temperatures from the kinetic reactions by Sheng et al. (9) and Sheldon (3).

If the molybdenum(VI) species is rapidly formed with $t-BuO_2H$ in the $MoO_2(acac)_2$ catalyzed oxidation, the reactivity difference of these systems in the dark and under light radiation can be explained by the nucleophilicity of the sulfide. The acceleration by the attack of sulfide under radiation caused the difference.

The third order rate constants (Table 7, Runs 43-47, 173) of the $MoO_2(acac)_2$ -catalyzed oxidation of PhSMe with $t-BuO_2H$ indicate that the oxidation reactions proceed smoothly under normal laboratory light conditions with any effect from the light which comes through the window.

But the irreproducibility of the $Mo(CO)_6$ catalyzed oxidation of PhSMe at $35^\circ C$ under normal light conditions indicates that any slight changes in light conditions affect the rate of oxidation.

II. The epoxidation of 1-octene

The epoxidation of 1-octene was accomplished in the presence of either Mo(CO)_6 or $\text{MoO}_2(\text{acac})_2$ at 85°C in benzene, under various light conditions. The primary reason for carrying out these reactions was to see the light effect on the reaction by changing the nucleophilic substrate. The system chosen was similar to that used by Sheng and Zajacek (2). The kinetic data were obtained by measurement of changes in $t\text{-BuO}_2\text{H}$ concentration with iodometric titration, and changes in 1-epoxyoctane by gas-liquid chromatography (Fig. 5). Reactions were carried out in a large excess of 1-octene. The decomposition of $t\text{-BuO}_2\text{H}$ is assumed to be insignificant. The pseudo-first order kinetics were observed (Fig. 6) in Mo(CO)_6 -catalyzed epoxidation. The kinetic data (Table 4) fit the following rate law which is shown in Equation 53.

$$\text{Rate} = k[\text{1-octene}][t\text{-BuO}_2\text{H}][\text{Mo(CO)}_6] \quad (53)$$

(First order dependency on each reactant was reported by Sheng (2).)

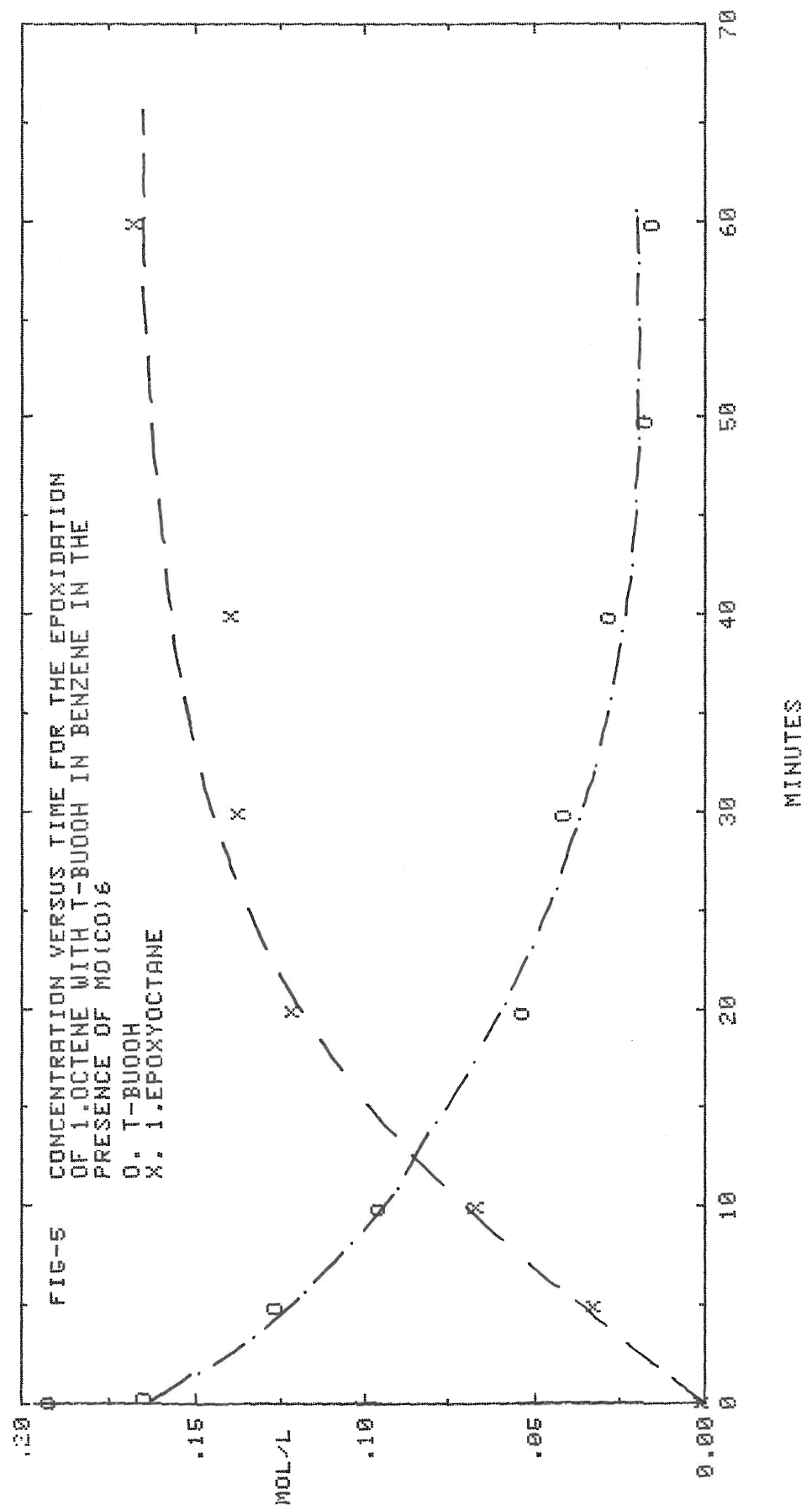
The reactions were done in the dark, under normal light conditions and under UV radiation. The third order rate constants indicate that the reactions proceed at the same rate either in the dark or under normal light, whereas under UV radiation, the reaction proceeds 4.6 times faster than in the dark and under normal light. These data show that the oxidation of molybdenum(0) to molybdenum(VI) with $t\text{-BuO}_2\text{H}$ and the formation of hydroperoxide-olefin-molybdenum complexes occur at high temperatures. It seems to be the case that UV light accelerates the attack of the double bond to the electropositive oxygen on the hydroperoxide-containing complex.

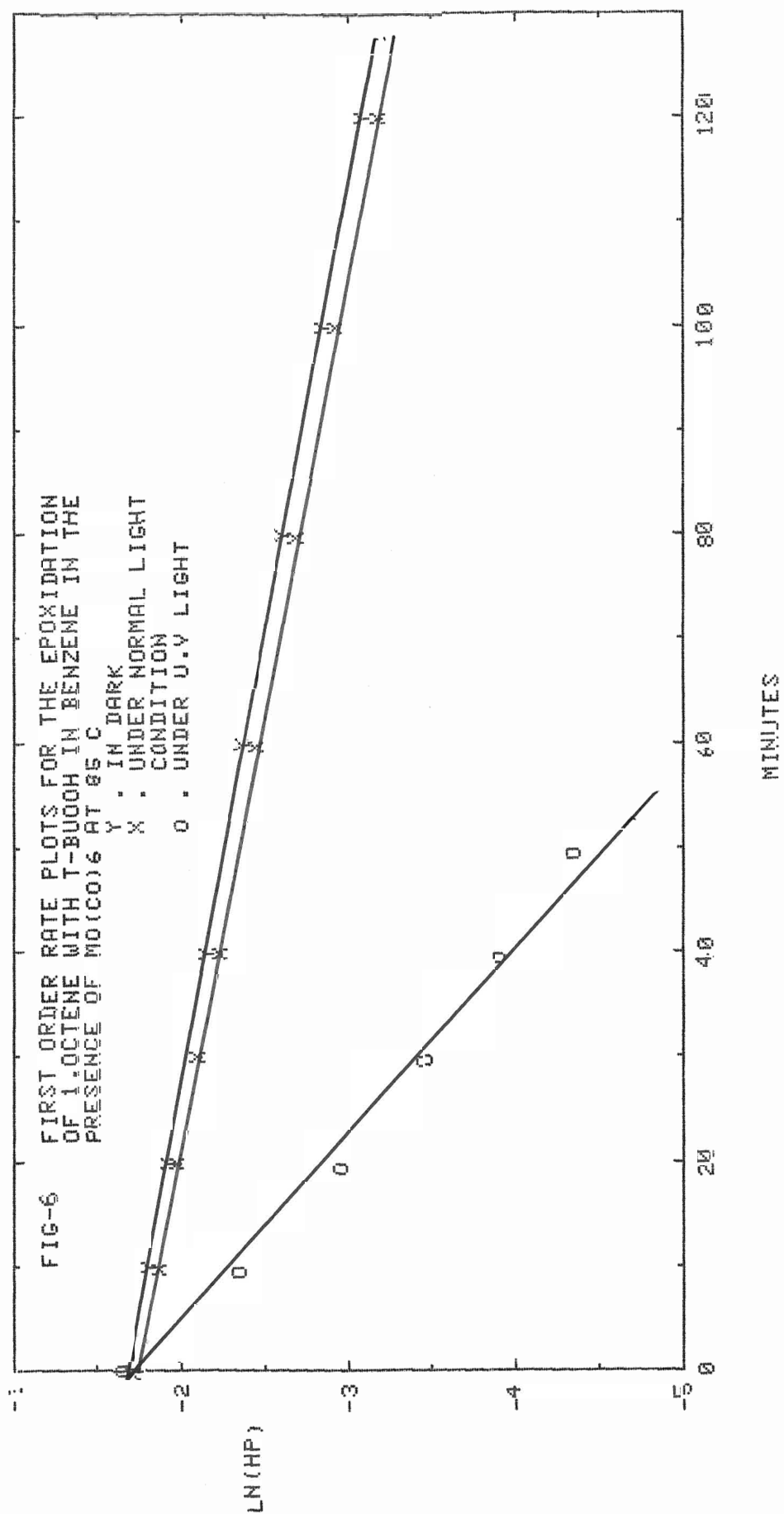
Table 4. The epoxidation of 1-octene by t-BuO₂H in the presence of Mo(CO)₆ and MoO₂(acac)₂ under various light conditions.^a

Run Number	[1-octene]	[t-BuO ₂ H]	Catalyst	[cat] x 10 ⁵	T°C	Light conditions	k ₁ min ⁻¹	k ₂ M ⁻¹ min ⁻¹	k ₃ M ⁻² min ⁻¹
98	2.626	0.1820	Mo(CO) ₆	12.68	85	UV	0.05164	0.0196	155.02
99	2.626	0.1813	Mo(CO) ₆	11.89	82	UV	0.4650	0.0177	149.15
100	2.588	0.1773	Mo(CO) ₆	11.89	85	normal	0.01035	0.00400	33.65
101	2.588	0.1785	Mo(CO) ₆	12.41	85	dark	0.01130	0.00460	37.35
102	2.588	0.1776	Mo(CO) ₆	11.79	85	normal	0.01147	0.00433	37.61
114	2.626	0.1816	MoO ₂ (acac) ₂	11.75	85	UV	0.1543 0.04440 ^b	0.0587 0.0169 ^b	499.70 143.72 ^b
115	2.626	0.1850	MoO ₂ (acac) ₂	11.61	85	normal	0.1220 0.03743 ^b	0.0464 0.01425 ^b	399.84 122.67 ^b
161	2.512	0.1740	MoO ₂ (acac) ₂	12.22	85	dark	0.1189 0.03454 ^b	0.0473 0.0138 ^b	387.14 110.87 ^b

^a under air atmosphere

^b final rates





The difference between sulfide oxidation and olefin epoxidation were the reaction temperatures. At high temperatures, catalyst has enough energy to activate itself. But at low temperature, more energy (which comes from UV light) is required to activate the catalyst.

As mentioned earlier, the formation of molybdenum-olefin-hydroperoxide complexes occurs when the molybdenum is in the 6+ oxidation state. Since the molybdenum(VI) is a stronger Lewis acid than the molybdenum(0), the formation of such complexes must be in favour of the 6+ oxidation state of molybdenum. However, no such complexes could be obtained in this work.

Previously, the formation of the complexes between Mo(CO)_6 and either various olefins or alcohols under UV radiation were observed and characterized by their IR spectra by various authors (60-65). The formation of $\text{Mo(CO)}_5\text{SPh}_2$ and $\text{Mo(CO)}_5\text{S(CH}_3)_2$ complexes were also observed and characterized by their IR and NMR spectra by Herberhold et al. (66). It has been suggested that olefins or alcohols can replace only one carbonyl group due to back charge acceptor ability of these ligands. However, di- and tri-substituted complexes can be obtained, but they are very unstable and more energy is required. Experiments were therefore done to observe the complexation between Mo(CO)_6 and 1-octene by IR spectroscopy. The hypothesis was that if $\text{Mo(CO)}_6\text{-x}^+\text{1-octene}_x$ complex could be obtained in the zero oxidation state of molybdenum, the formation of these complexes with molybdenum must be formed in the 6+ oxidation state.

Table 5 lists the conditions and IR stretching frequency of the CO group in molybdenum complexes. From spectral analysis, the $\text{Mo(CO)}_5\text{-1-octene}$ complex could be obtained at either 85°C, or 85°C and under UV radiation

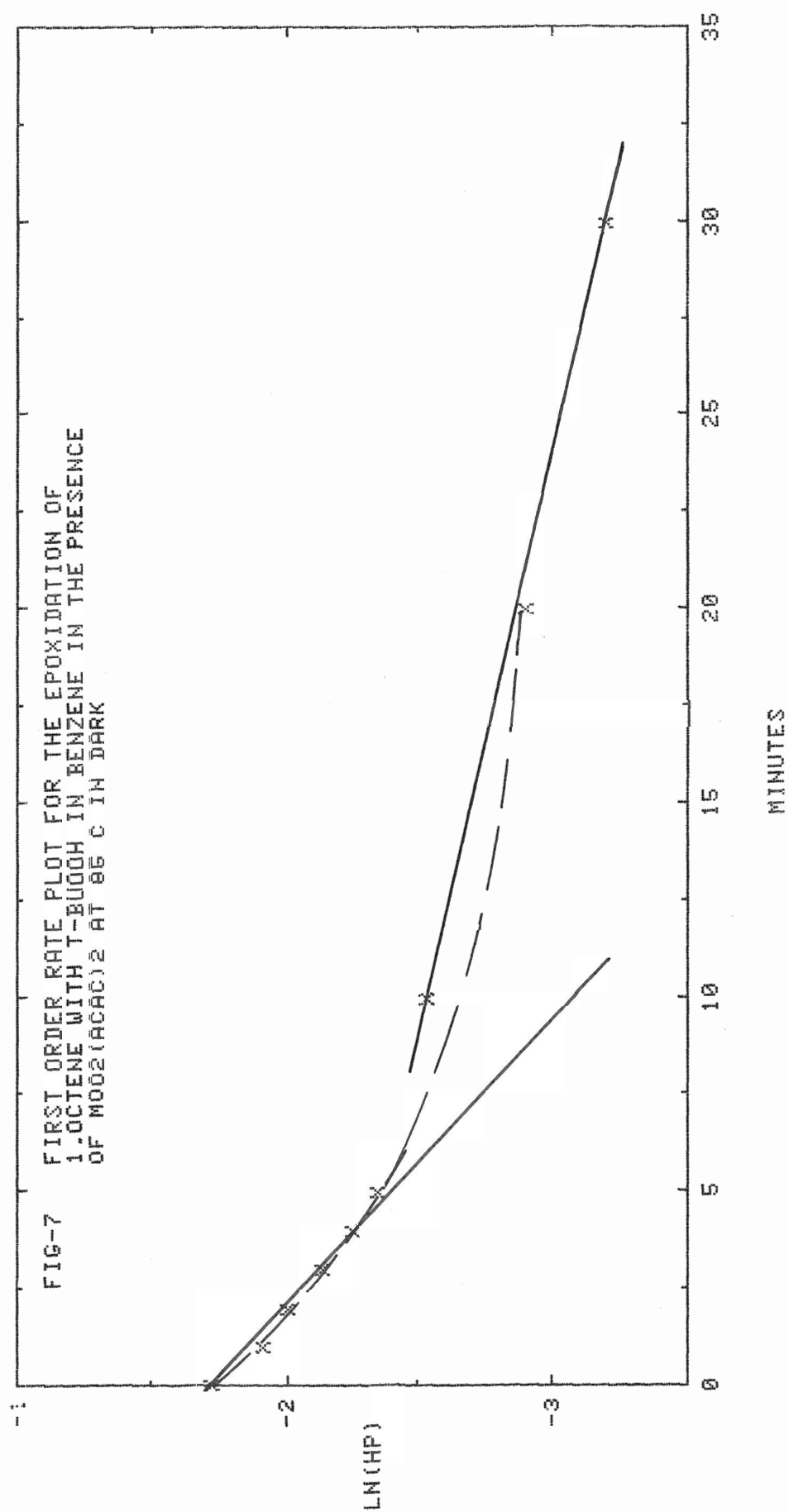
Table 5. Carbonyl stretching frequencies of Mo(CO)_6 under various conditions.

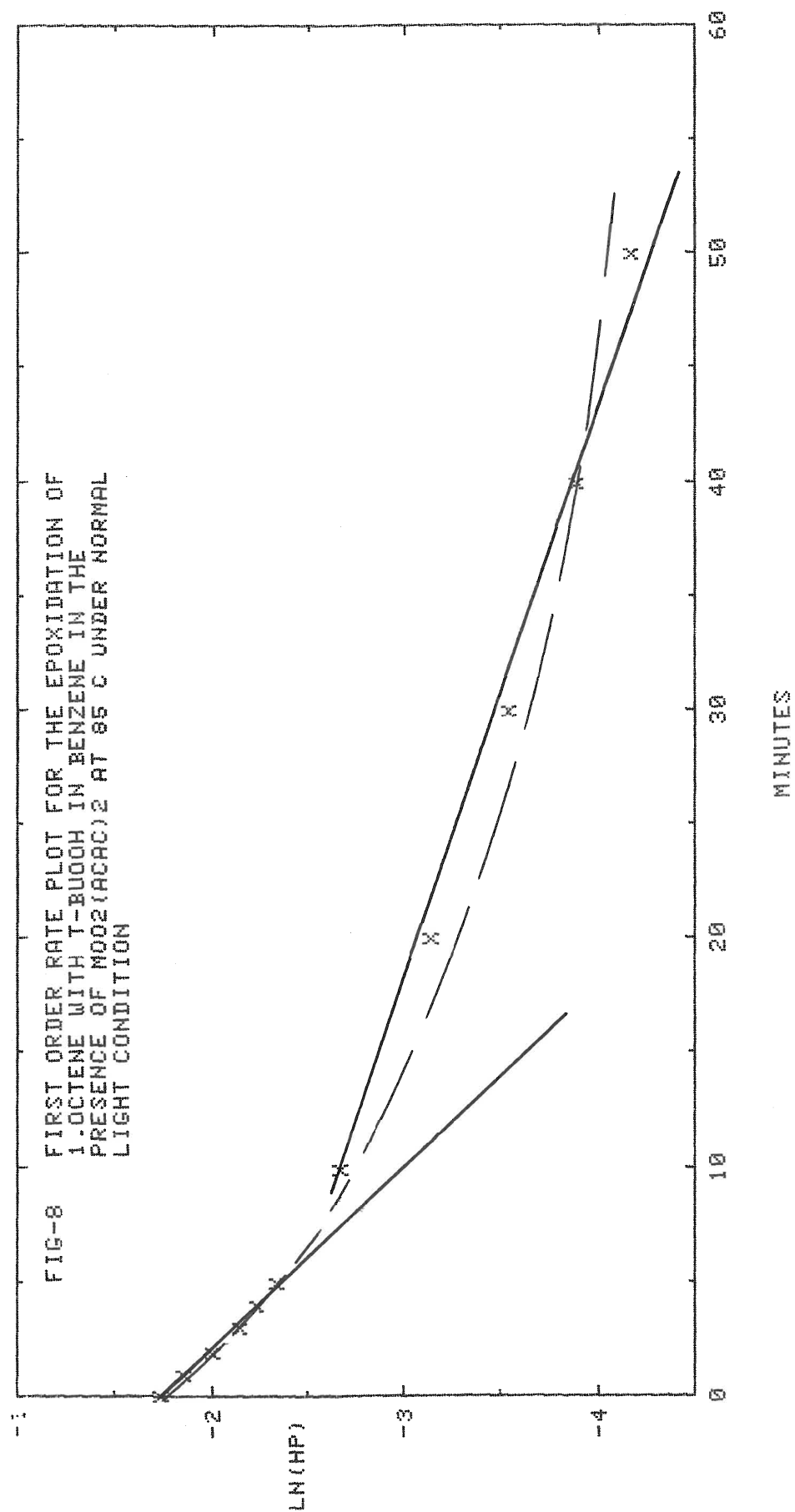
Spectrum Number	Compounds	Light Condition	Heat Condition	$\nu \text{ cm}^{-1}$
7	1-octene + Mo(CO)_6	UV 10 min	85°C	1990(s) 1955(m) 1821(m)
8	1-octene + Mo(CO)_6	--	85°C 5 min	1987(s) 1955(m) 1820(m)
9	1-octene + Mo(CO)_6	--	--	1987(s)
10	1-octene	--	--	--

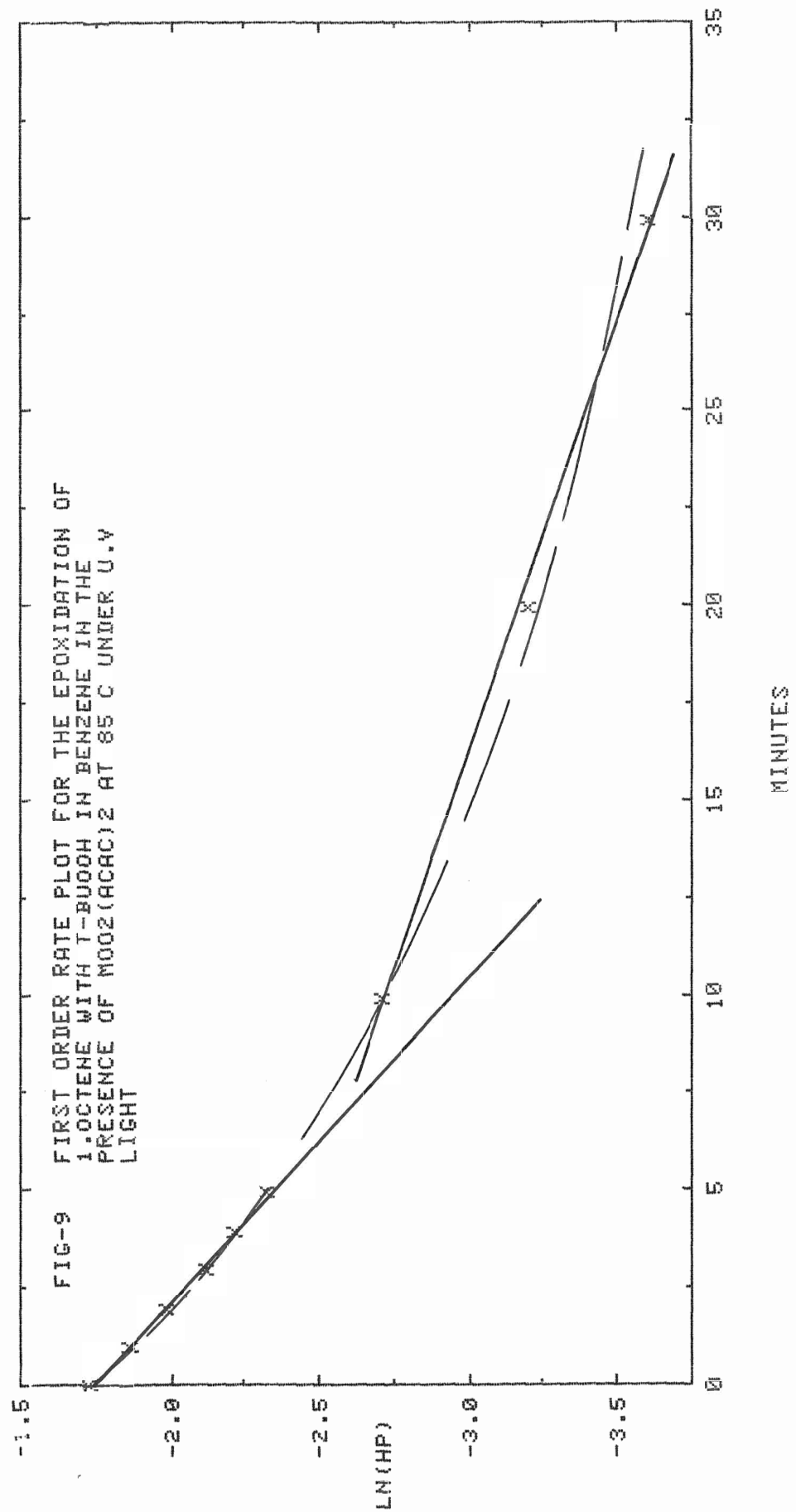
(Appendix 4). The spectrum in the carbonyl stretching region of the infrared for this type of monosubstituted complex is characteristic of the replacement of one CO group of an octahedral complex leaving a square pyramid carbonyl about the metal. Such a spectrum should contain three carbonyl stretching bands. The IR spectrum of Mo(CO)_5 -1-octene (Appendix 6) consists of three bands at 1980 cm^{-1} (s) (corresponding to an E band) and $1955, 1821\text{ cm}^{-1}$ (m) corresponding to two A_1 bands). The IR spectrum of Mo(CO)_6 in 1-octene at room temperature gives one band at 1987 cm^{-1} (s). This corresponds to the T_{1u} band in Mo(CO)_6 .

The formation of the same complex at either high temperatures or high temperatures and UV radiation indicates that heat is a sufficiently strong energy source to activate the catalyst. According to kinetic and IR experiments, it can be concluded that UV light has an accelerating effect on the attack of the double bond.

The epoxidation was also carried out in the presence of $\text{MoO}_2(\text{acac})_2$ under different light conditions. Kinetic data (Figs. 7-9) show that $\text{MoO}_2(\text{acac})_2$ behaves differently from Mo(CO)_6 in the epoxidation reaction. $\text{MoO}_2(\text{acac})_2$ gave a higher rate of epoxidation initially, then the rate decreased with time. The same observation was made by Sheldon (12). The present results, however, are in contrast with his results; since it has been observed that after differing initial rates, the reactions proceed with the same rate in the presence of various molybdenum catalysts, including Mo(CO)_6 and $\text{MoO}_2(\text{acac})_2$. In this work, the final rates of $\text{MoO}_2(\text{acac})_2$ -catalyzed epoxidations are not similar to those found in the Mo(CO)_6 -catalyzed epoxidation under either dark or normal light conditions (except for the reaction done under UV radiation).







III. The Mo(CO)_6 -catalyzed epoxidation of 1-octene in the presence of phenylmethyl sulfide

The effect of sulfide as a co-catalyst in the Mo(CO)_6 -catalyzed epoxidation of 1-octene by $t\text{-BuO}_2\text{H}$ in benzene and ethanol was studied. The reaction was followed by iodometric titration of $t\text{-BuO}_2\text{H}$ and by gas-liquid chromatography analysis of 1-epoxyoctene (Fig. 10). A stoichiometry of 1:1 was obtained for each reaction and pseudo first order kinetics were observed for the epoxidation reaction (Fig. 11). On the assumption that sulfide is required to activate the catalyst, 0.1 M of phenylmethyl sulfide was added to the initial reaction mixture. In contrast to the expected result, kinetic data in Table 6 show that in the presence of sulfide, the rate of epoxidation in benzene decreased. The amount of phenylmethyl sulfide was lowered by 50% and the rate of epoxidation reaction showed an increase. It seemed that in spite of sulfide, sulfoxide or probably sulfone had an effect in these reactions, because sulfide was oxidized to sulfoxide very rapidly in this reaction system. The disappearance of sulfoxide was observed to occur in 20 minutes, after which epoxidation reaction started and continued in the presence of sulfone.

Changing the solvent from benzene to ethanol decreased the epoxidation rate by a factor of 2.5. The effect of alcoholic solvent can be ascribed to the following factors:

- (i) competitive complexation of alcohols and $t\text{-BuO}_2\text{H}$ with molybdenum,
- (ii) involvement of ethanol in the transition state.

The solvent effect was reserved for later discussion.

Table 6. Mo(CO)_6 -catalyzed epoxidation of 1-octene by $t\text{-BuO}_2\text{H}$ in the presence of phenylmethyl sulfide.^{a,b}

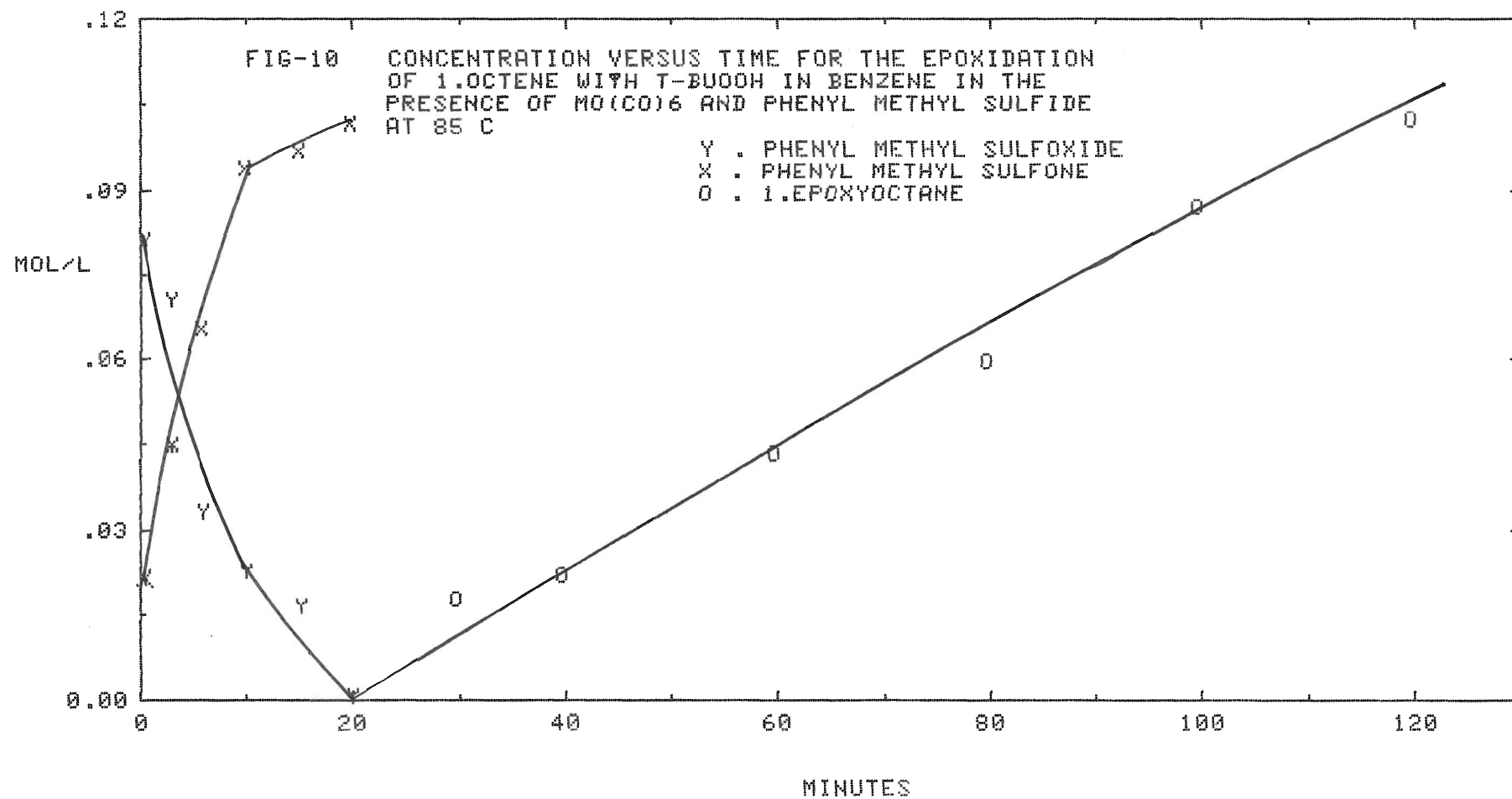
Run Number	[1-octene]	[PhSMe]	[$t\text{-BuO}_2\text{H}$]	[Mo(CO)_6] $\times 10^5$	Solvent	k_1^c min^{-1}	k_2^c $\text{M}^{-1} \text{min}^{-1}$	k_3^c $\text{M}^{-2} \text{min}^{-1}$	k^d $\text{M}^{-2} \text{min}^{-1}$
104	2.375	0.101	0.500	10.917	benzene	0.00384	0.00162	14.84	3621
106	2.375	0.101	0.502	11.073	benzene	0.00380	0.00160	14.45	3061
107	2.375	0.0510	0.502	11.519	benzene	0.0515	0.00217	18.85	4779
108	2.375	0.101	0.504	11.480	ethanol	0.00155	0.000565	5.700	1353

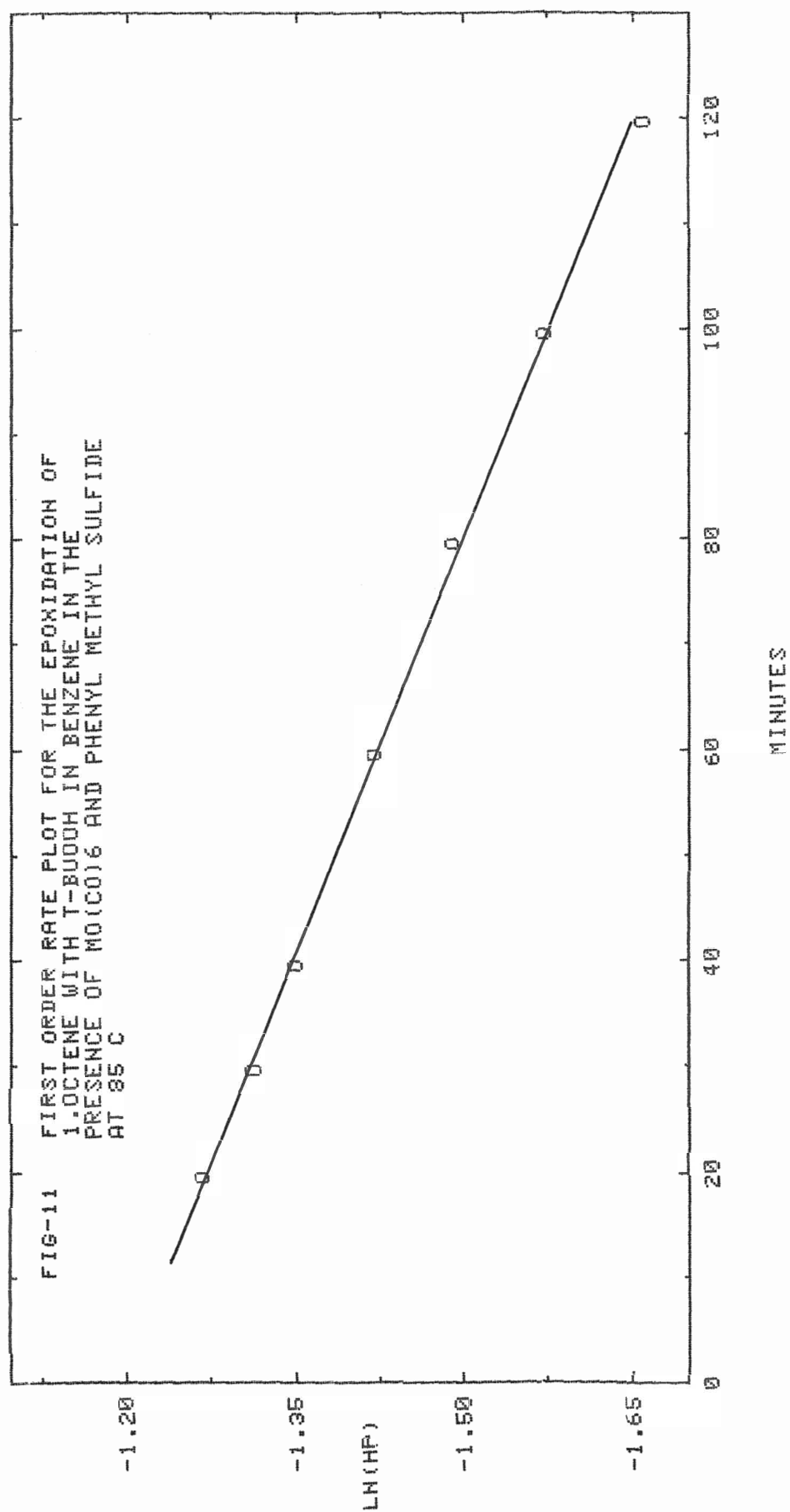
^a under normal light conditions.

^b at 85°C under air atmosphere

^c the rates of epoxidation

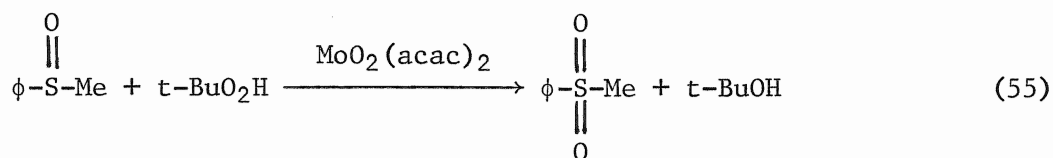
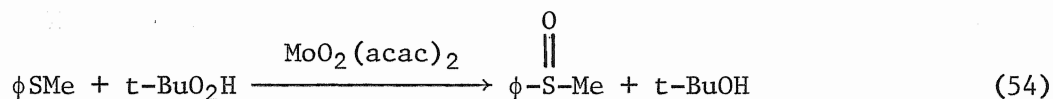
^d the oxidation rate of sulfoxide





IV. The oxidation of phenylmethyl sulfide and substituted phenylmethyl sulfides

The oxidations of phenylmethyl sulfide with $t\text{-BuO}_2\text{H}$ were carried out over a temperature range of $27\text{--}45^\circ\text{C}$ in ethanol in the presence of $\text{MoO}_2(\text{acac})_2$. Phenylmethyl sulfoxide and t -butyl alcohol were obtained as products. Since the molar ratio of sulfide to hydroperoxide was 5:1, the oxidation of phenylmethyl sulfoxide to phenylmethyl sulfone did not proceed. The loss of sulfide and the formation of sulfoxide showed a 1:1 stoichiometric relationship. But, as observed by Köseoğlu (46), when the sulfide:hydroperoxide molar ratio of 1:1 or 1:2 was employed, both reactions, the oxidations of sulfide to sulfoxide, and the oxidations of sulfoxide to sulfone, were observed (Eqs. 54, 55).



In most cases, the sulfide:hydroperoxide molar ratio of 5:1 was employed in order to eliminate the sulfoxide oxidation.

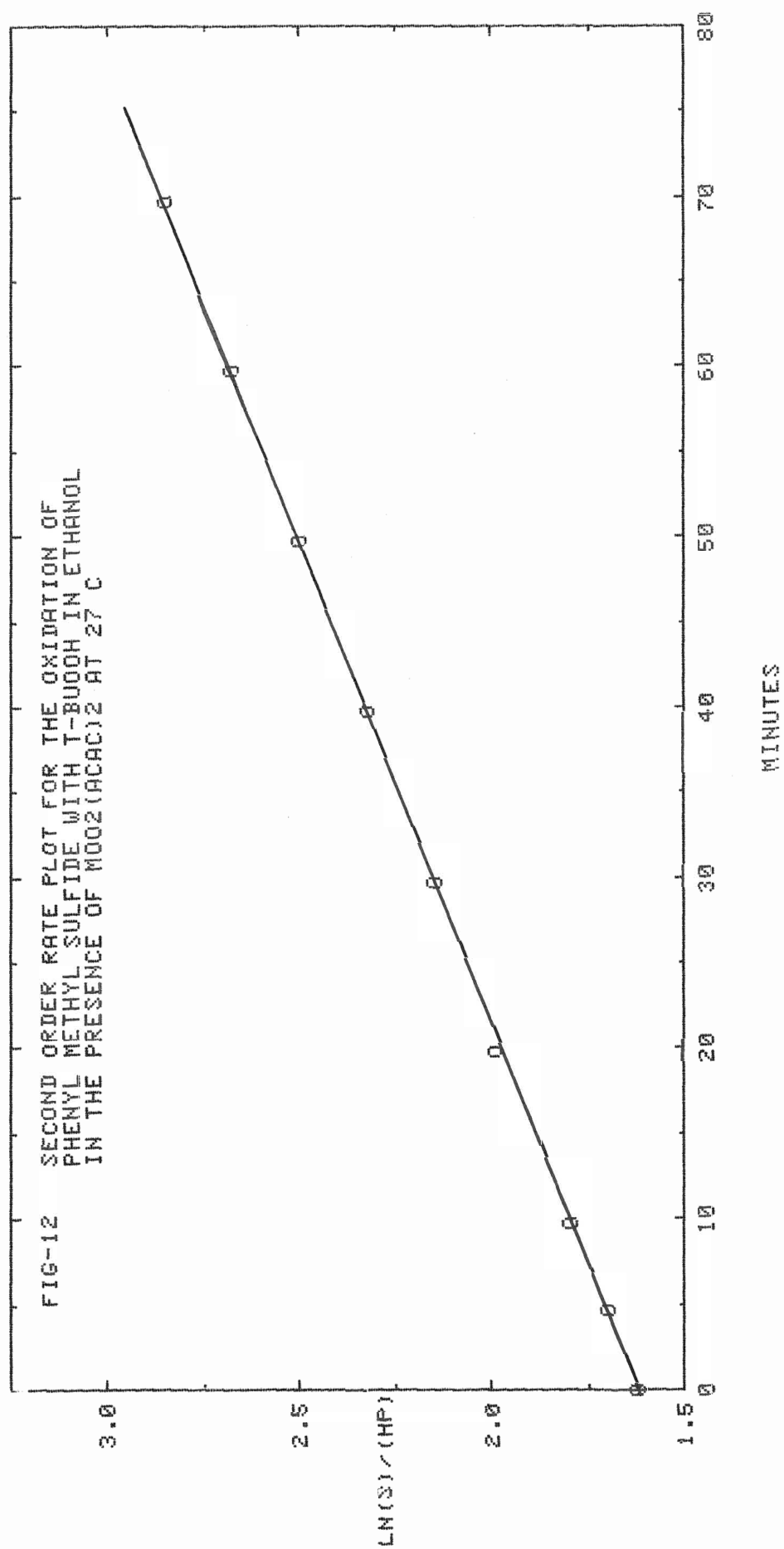
The reaction was followed by monitoring the disappearance of t -butyl hydroperoxide by iodometric titration. The obtained data fit Figure 12, the second order rate law that is shown in Equation 5, since there is no decomposition of $t\text{-BuO}_2\text{H}$ at the low concentration of catalyst, and there is no uncatalyzed oxidation of sulfide.

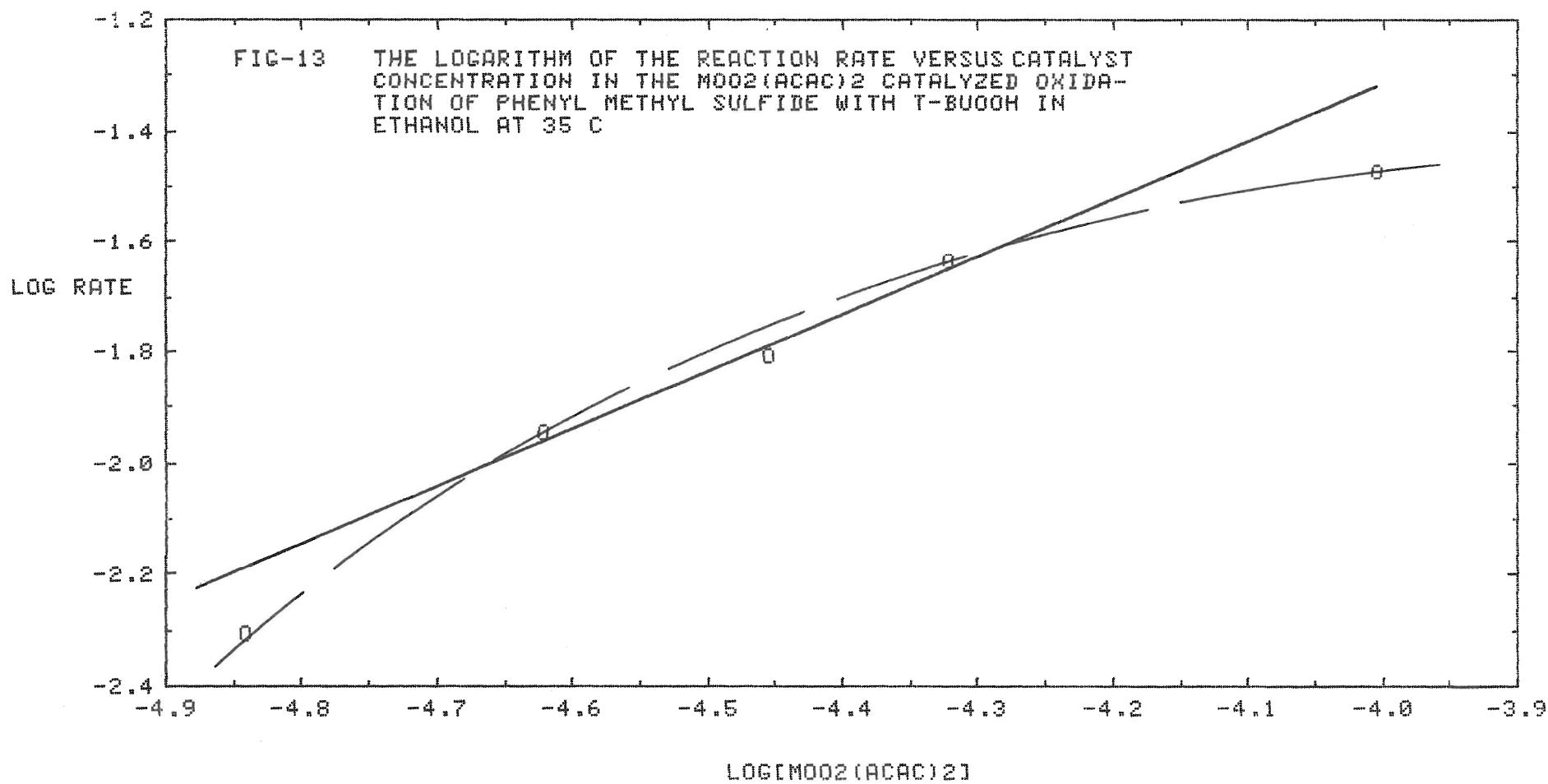
Table 7. $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of phenylmethyl sulfide with $t\text{-BuO}_2\text{H}$ in ethanol.^a

Run Number	$[\phi\text{SMe}]$	$[t\text{-BuO}_2\text{H}]$	$[\text{MoO}_2(\text{acac})_2] \times 10^5$	$T^\circ\text{C}$	$k_2 \text{ M}^{-1} \text{ min}^{-1}$	$k_3 \text{ M}^{-2} \text{ min}^{-1}$
53	1.005	0.205	2.407	35	0.05490	2279
56	1.003	0.204	2.638	27	0.02216	840
59	1.009	0.202	2.233	45	0.1096	4908
50	1.007	0.103	5.084	35	0.1205	2371
51	1.005	0.103	4.562	35	0.1035	2268
52	1.001	0.205	4.792	35	0.1131	2360
47	1.003	0.202	9.960	35	0.1650	1660
46	1.000	0.203	9.770	35	0.1680	1724
45	1.003	0.202	9.608	35	0.1640	1714
44	1.000	0.202	9.540	35	0.1630	1709
43	1.000	0.200	9.570	35	0.1550	1623
54	1.005	0.202	1.450	35	0.02450	1664
171	1.002	0.208	3.528	35	0.07419	2120
173 ^b	1.022	0.209	3.396	35	0.07930	2335

^a under nitrogen atmosphere

^b run done at night





$$\text{Rate} = k_2[\phi\text{SMe}][t\text{-BuO}_2\text{H}] \quad k_2 = k_3[\text{cat}] \quad (56)$$

The results of kinetic measurements are given in Table 7. The values at 35°C show that the reaction order with respect to the catalyst is approximately first order within the range 2.407×10^{-5} – 4.792×10^{-5} M (Fig. 13). Deviation was observed at a higher or lower concentration of the catalyst. Furthermore, the first order dependency on $t\text{-BuO}_2\text{H}$ is observed.

The oxidations of $p\text{-CH}_3\text{O}$, $p\text{-CH}_3$, $p\text{-NO}_2$, $p\text{-H-C=O}$, $p\text{-CH}_3\text{C=O}$, $p\text{-Cl}$, $p\text{-Br}$ and $p\text{-OH}$ substituted phenylmethyl sulfide were also carried out using $t\text{-BuO}_2\text{H}$ in the presence of $\text{MoO}_2(\text{acac})_2$. The kinetic data are presented in Tables 8–10, and the oxidations follow second order kinetics for each of the substituted phenylmethyl sulfides (Figs. 14–21). The rate constants were calculated by using Equation 56.

Similar to phenylmethyl sulfide oxidation, the first order dependency on the catalyst is observed within the range of 1.29×10^{-5} – 4.73×10^{-5} M in the oxidation of $p\text{-methoxyphenylmethyl sulfide}$ (Fig. 22).

The third order rate constants for the oxidation of the substituted phenylmethyl sulfides were determined, assuming the first order dependency on catalyst similar to phenylmethyl sulfide and $p\text{-methoxyphenylmethyl sulfide}$.

The oxidations of $p\text{-acetyl}$ and $p\text{-nitrophenylmethyl sulfides}$ could not be run at 35°C due to poor solubilities of these compounds in ethanol. The reactions were therefore accomplished at high temperatures and the relative rate constants at 35°C were calculated from their Arrhenius plots (Figs. 26, 27).

Table 8. $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of p-methoxyphenylmethyl sulfide with t-BuO₂H in ethanol.^a

Run Number	$[\text{CH}_3\text{O}\phi\text{SMe}]$	$[\text{t-BuO}_2\text{H}]$	$[\text{MoO}_2(\text{acac})_2] \times 10^5$	T°C	$k_2 \text{ M}^{-1} \text{ min}^{-1}$	$k_3 \text{ M}^{-2} \text{ min}^{-1}$
62	1.004	0.2009	2.423	35	0.154	6357
41	1.000	0.2000	4.730	35	0.303	6424
63	1.003	0.2002	2.533	35	0.162	6409
65	1.004	0.2023	1.294	35	0.0780	6053
70	1.003	0.2016	2.742	26	0.0850	3101
71	1.004	0.2055	2.490	15	0.0290	1165
72	1.006	0.2044	2.490	30	0.107	4316
73	1.008	0.2078	2.435	21	0.0525	2158

^a under nitrogen atmosphere

Table 9. $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of p-methylphenylmethyl sulfide with t-BuO₂H in ethanol.^a

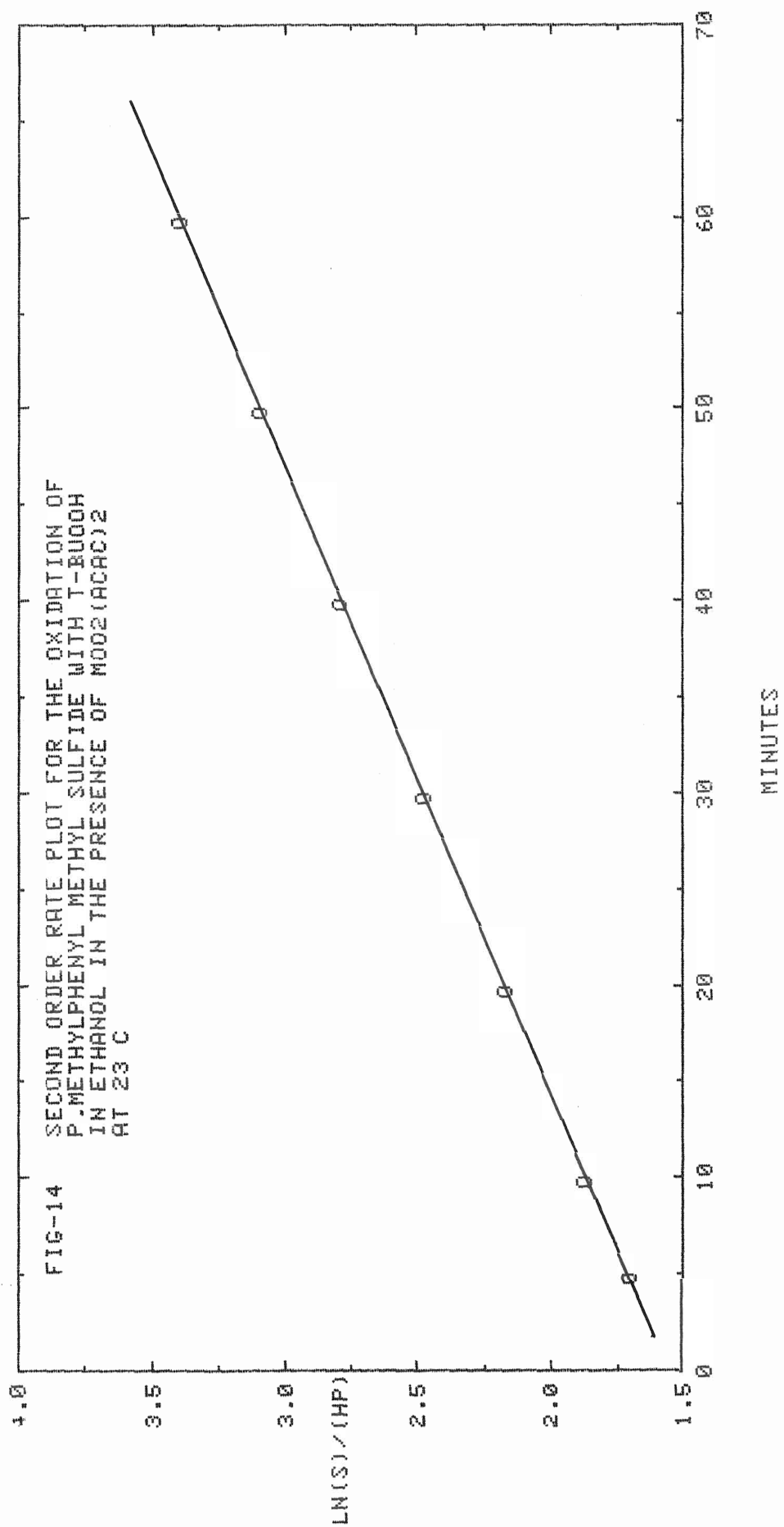
Run Number	$[\text{CH}_3\phi\text{SMe}]$	$[\text{t-BuO}_2\text{H}]$	$[\text{MoO}_2(\text{acac})_2] \times 10^5$	T°C	$k_2 \text{ M}^{-1} \text{ min}^{-1}$	$k_3 \text{ M}^{-2} \text{ min}^{-1}$
75	1.005	0.2041	2.450	35	0.1151	4551
87	1.007	0.2071	2.380	30	0.06540	2750
89	1.006	0.2089	2.362	26	0.04170	1765
90	1.005	0.2034	2.600	15	0.01490	573.9
91	1.001	0.2097	2.549	23	0.03280	1523

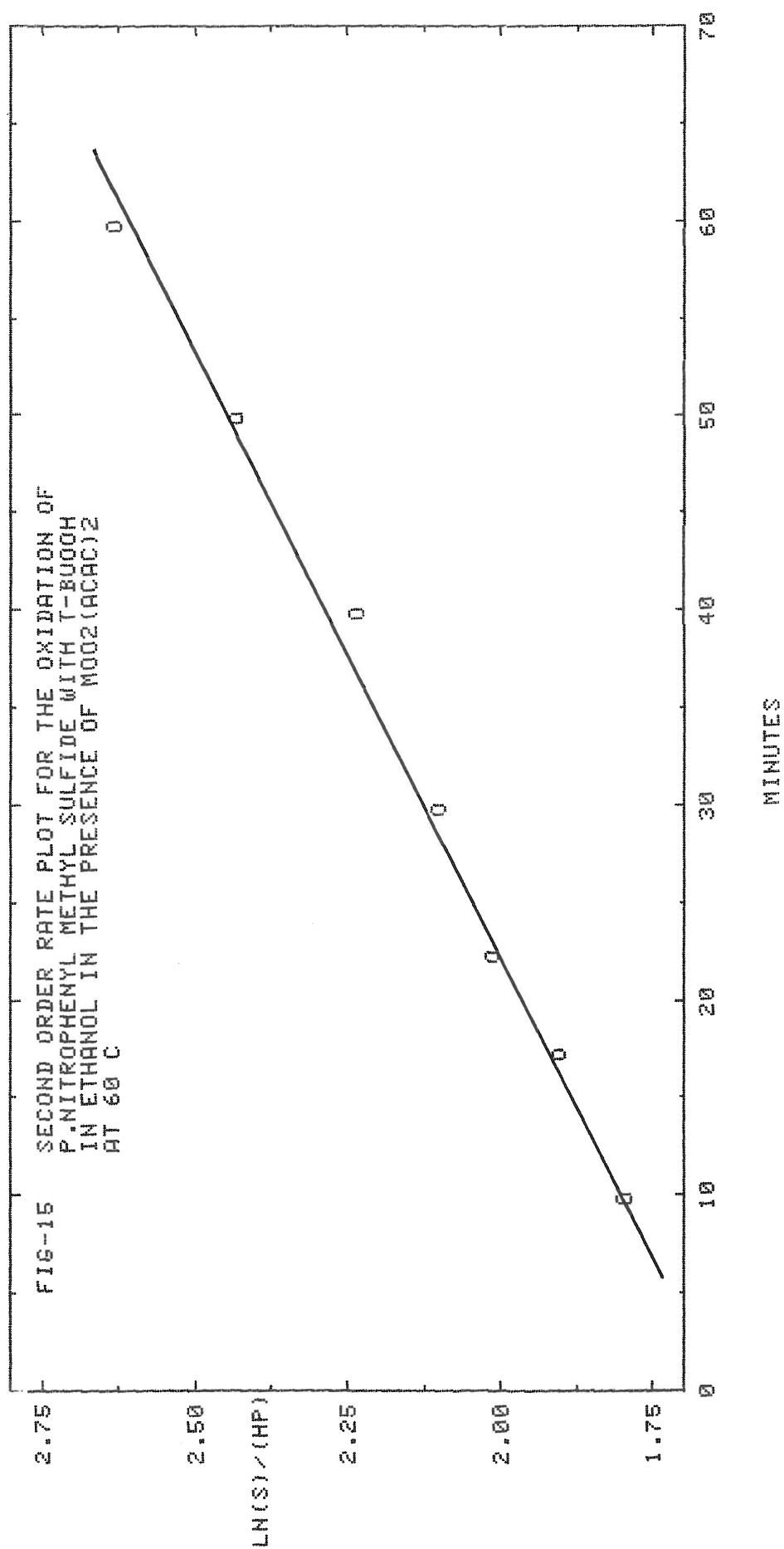
^a under nitrogen atmosphere

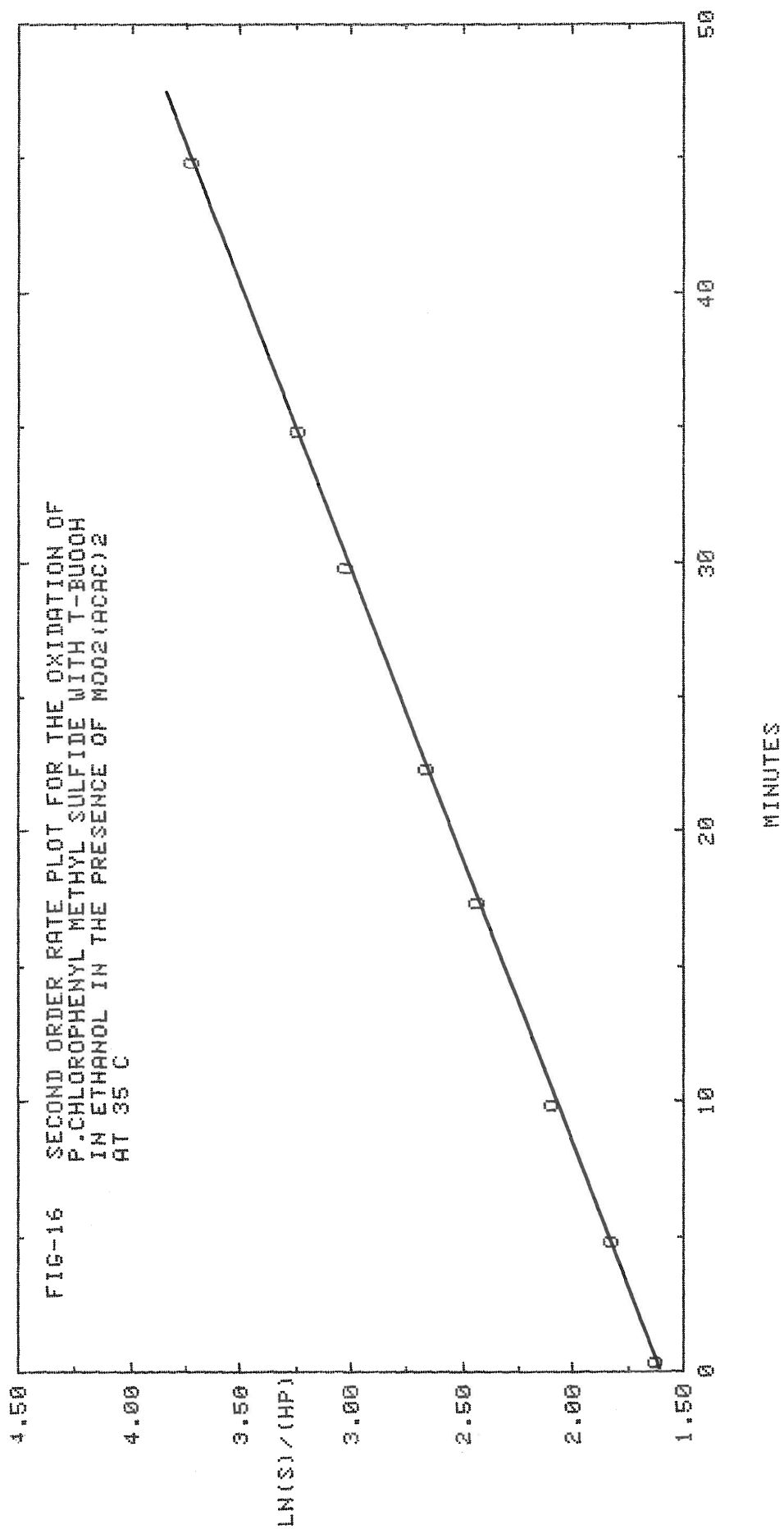
Table 10. $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of p-nitro-, p-chloro-, p-bromo- and p-hydroxy-phenylmethanethiols and p-methylthiobenzaldehyde with t-BuO₂H in ethanol.^a

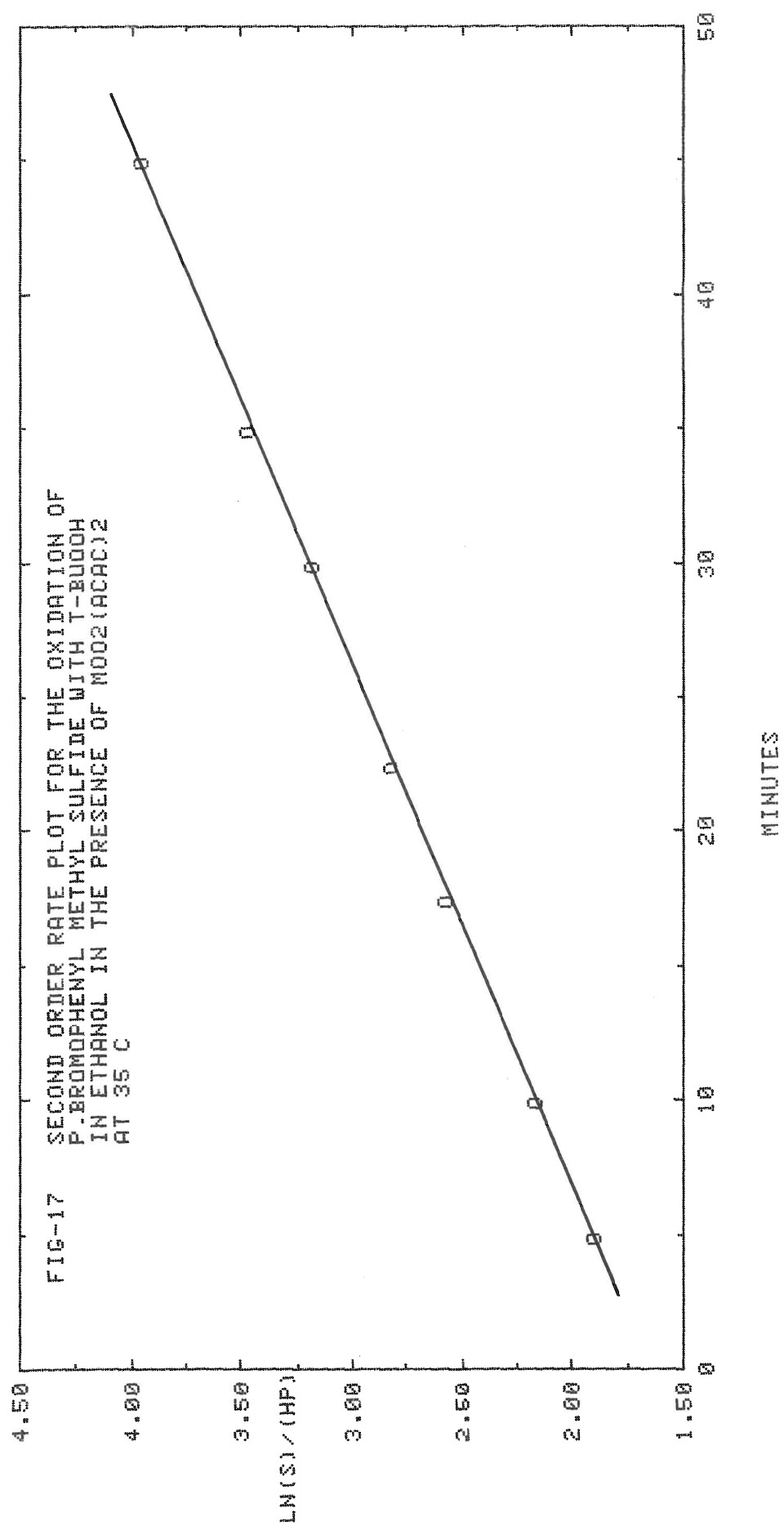
Run Number	X ———	[ϕSMe]	[t-BuO ₂ H]	[$\text{MoO}_2(\text{acac})_2$] $\times 10^5$	T°C	k_2 $\text{M}^{-1}\text{min}^{-1}$	k_3 $\text{M}^{-2}\text{min}^{-1}$
135	NO ₂	1.001	0.2063	2.463	70	0.05880	2387
136	"	1.001	0.2113	2.656	65	0.03875	1459
137	"	1.000	0.2096	2.619	75	0.08764	3346
144	"	1.000	0.2088	2.582	60	0.02060	798.0
139	Cl	1.000	0.2108	2.576	35	0.05970	2317
140	Br	1.002	0.2072	2.604	35	0.06470	2485
143	OH	1.002	0.2090	2.560	35	0.04260	1665
165	H-C=O	1.006	0.2031	2.607	35	0.007070	271
167	"	1.012	0.2035	2.776	35	0.007220	260
168	CH ₃ -C=O	1.006	0.2120	2.515	65	0.1262	5019
169	"	1.010	0.2085	2.546	70	0.2071	8134
170	"	1.002	0.2040	2.546	60	0.08085	3175

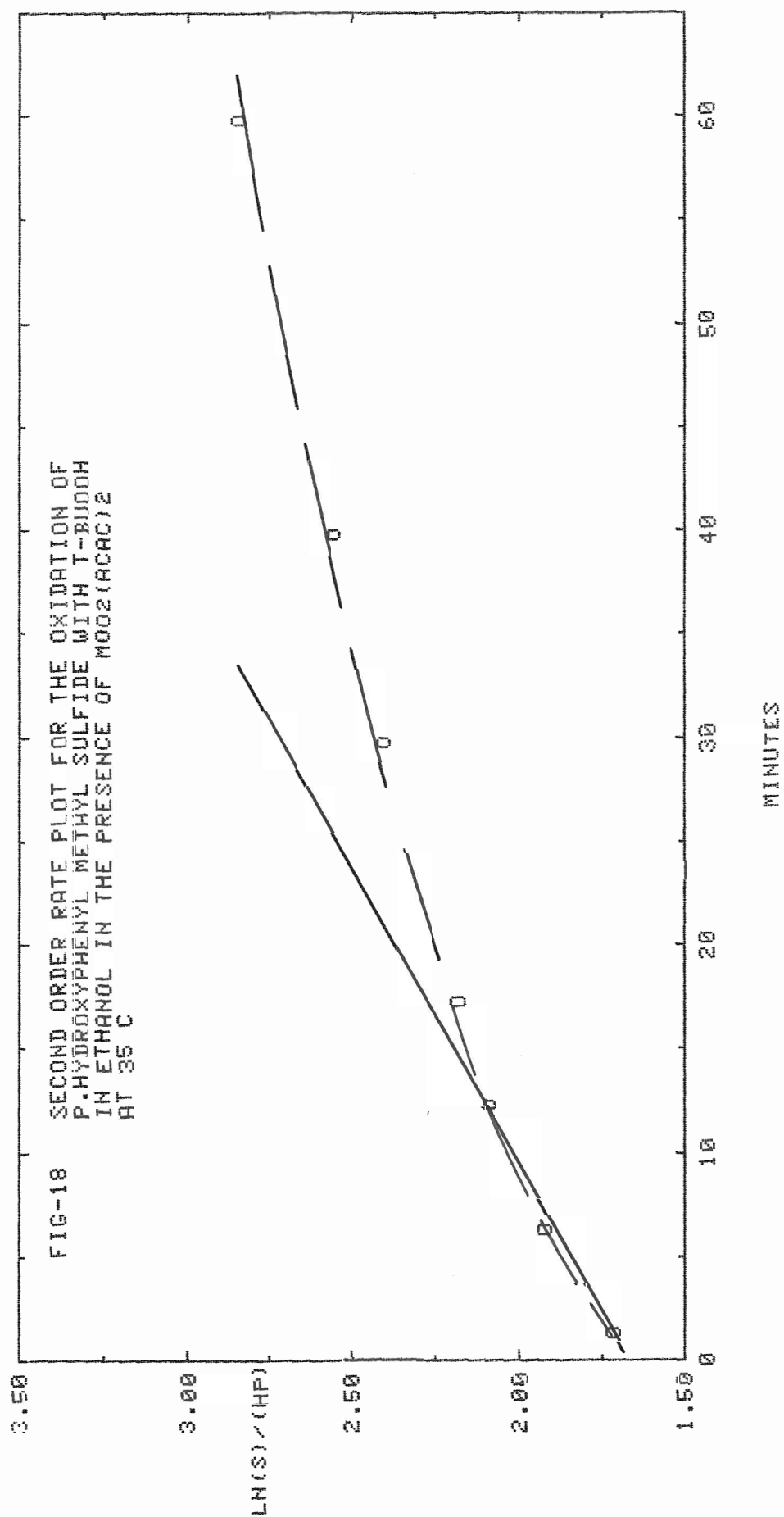
^a under nitrogen atmosphere

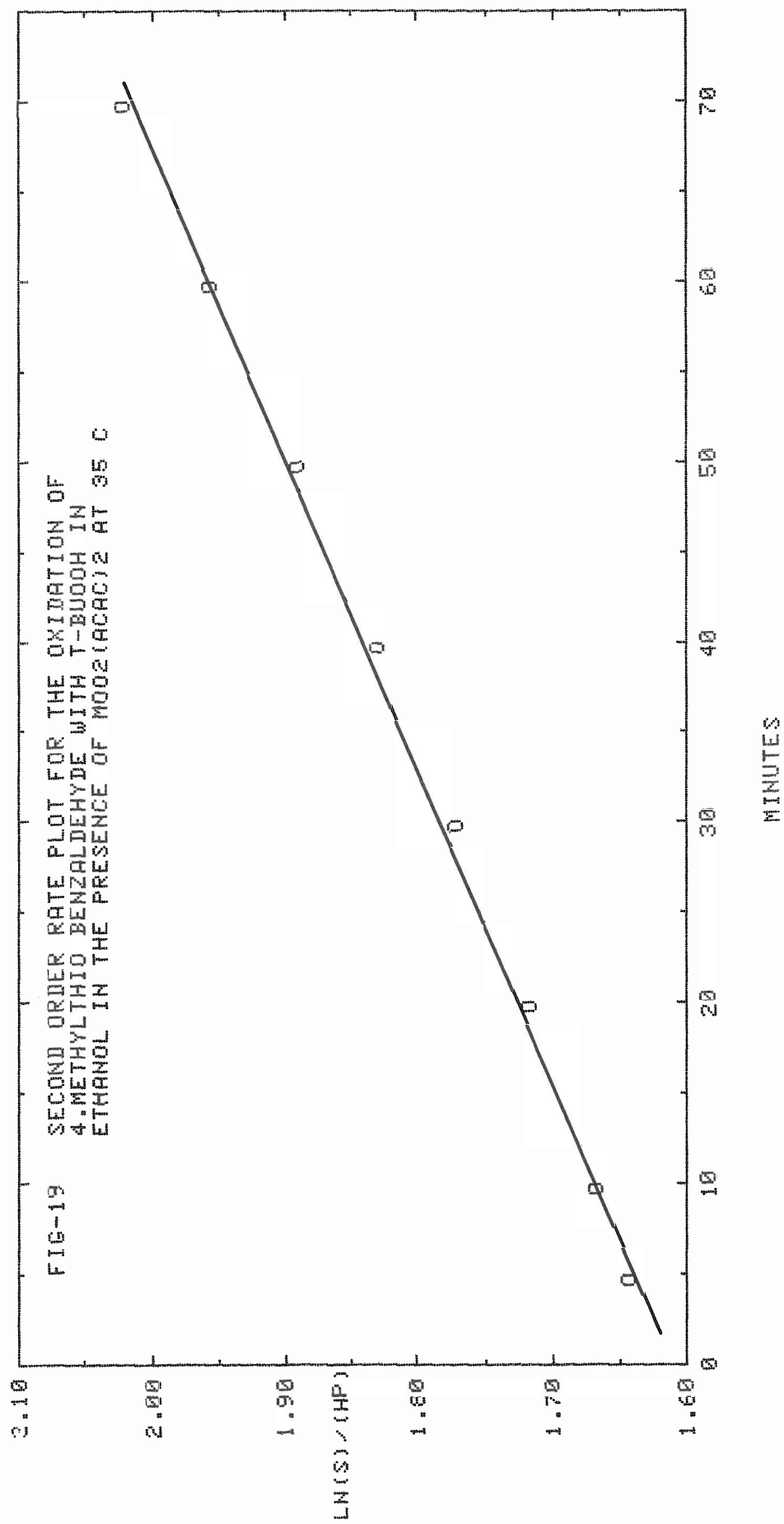


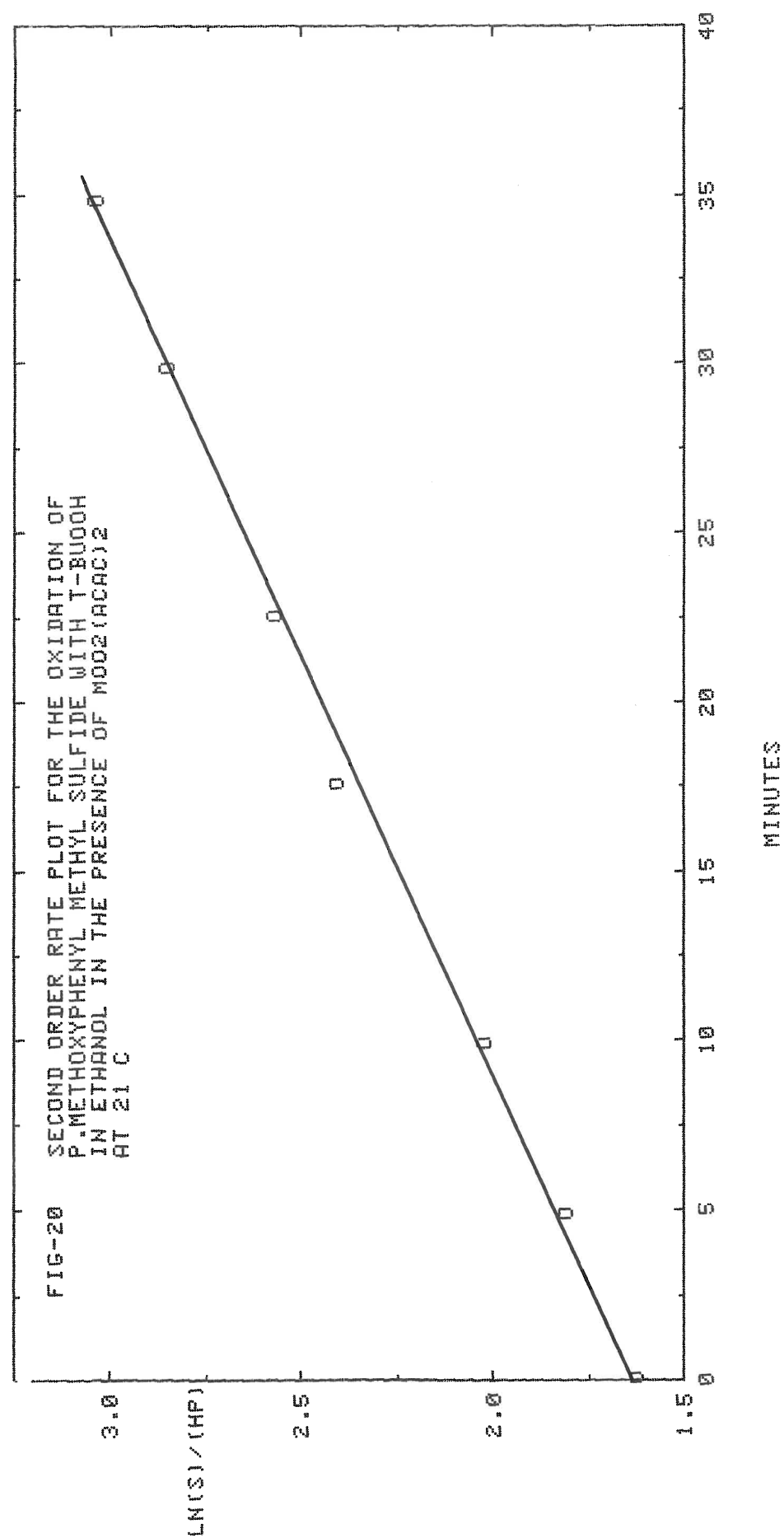


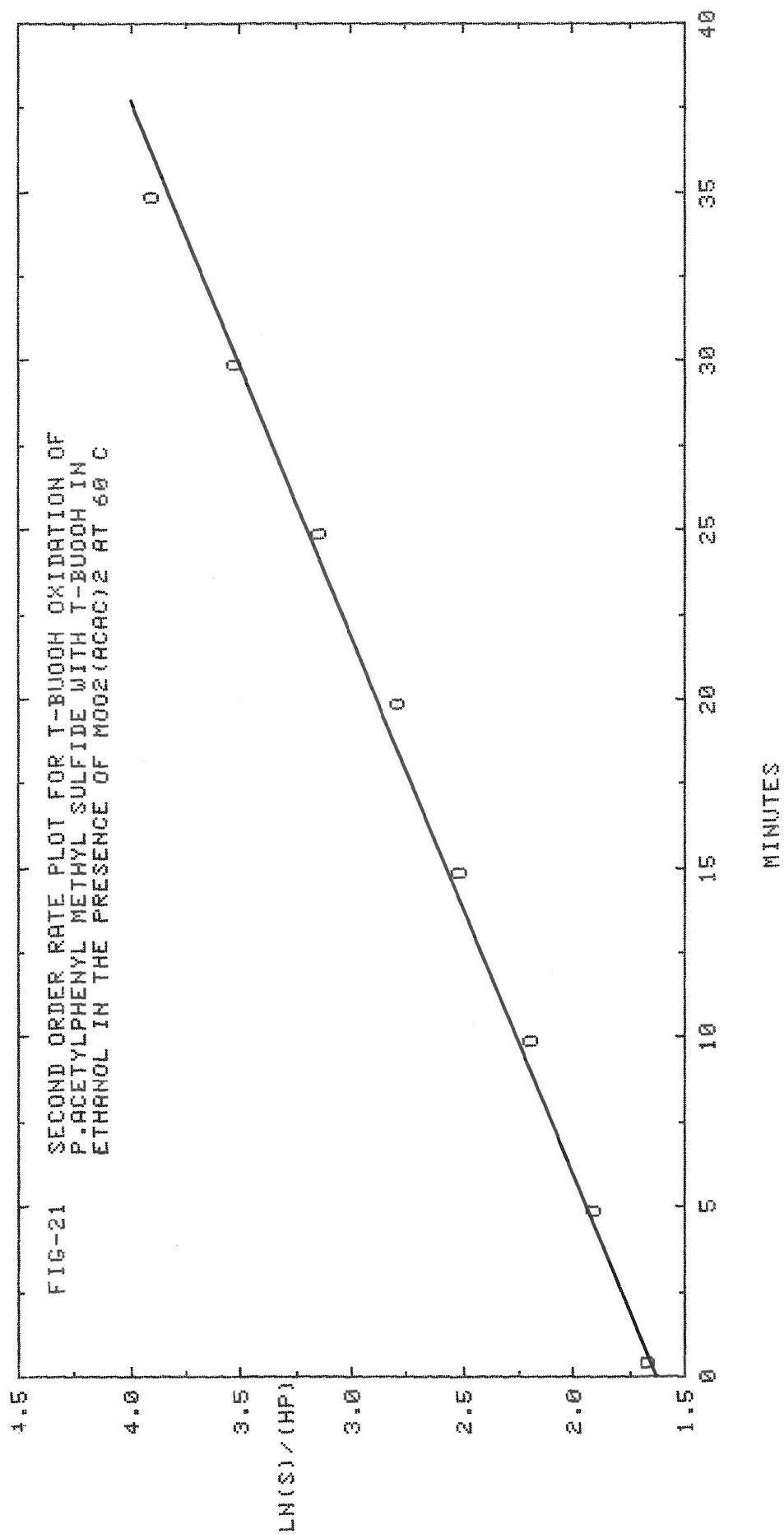


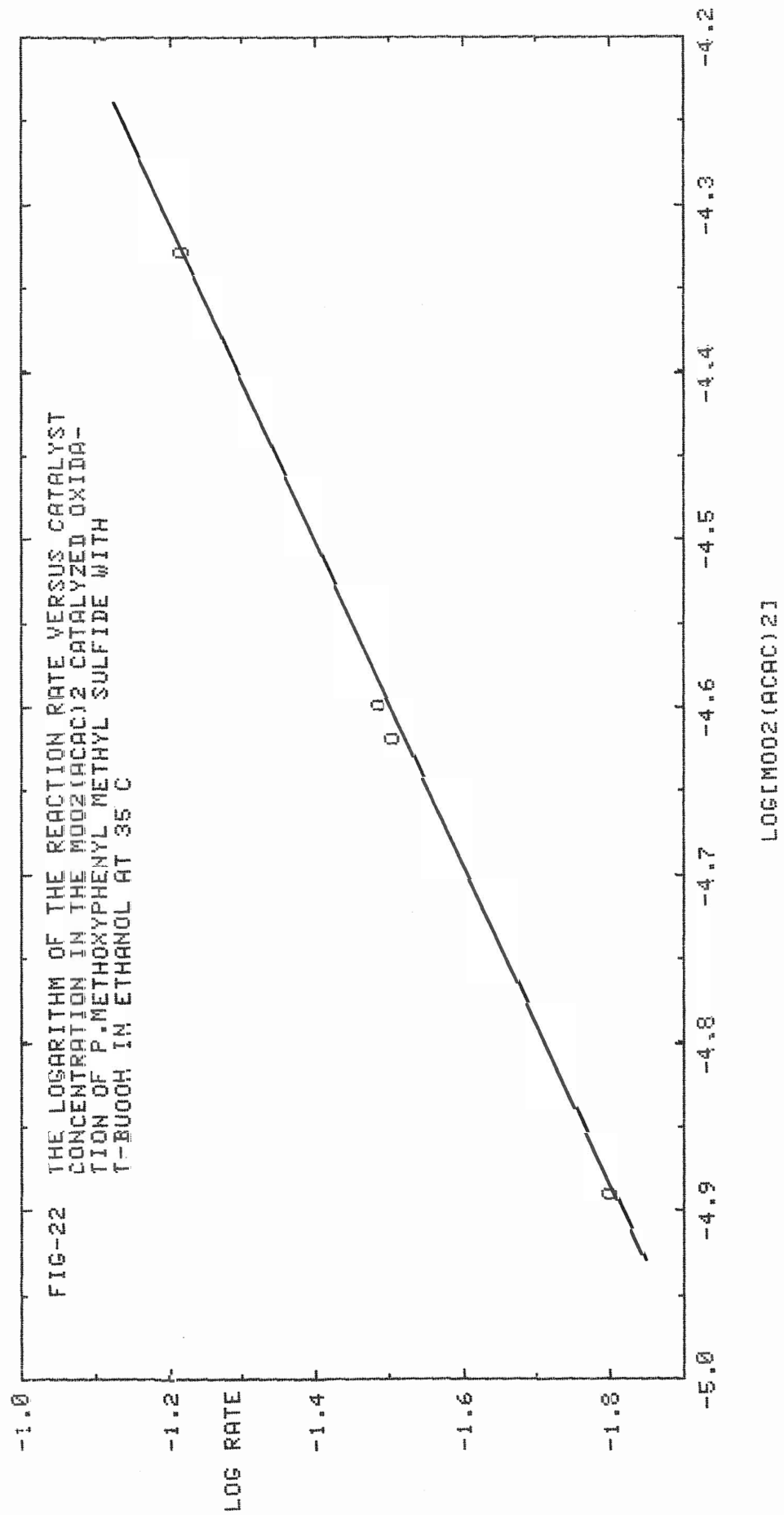












The Arrhenius plots (Figs. 23-29) of $\ln k_3$ versus $1/RT$ were linear and the activation energies were calculated from the slope of the straight lines. The intercept of these lines gives the $\ln A$ values. The activation energies of phenylmethyl sulfide, p-methoxy, p-methyl, p-nitro and p-acetyl phenylmethyl sulfides are summarized in Table 11. It is clearly seen that the activation energies are proportional to the substituent effects.

The electron donating groups, such as p-CH₃O and p-CH₃, increased the rate of reaction, while the electron attracting groups, such as p-NO₂, p-CH₃CO and p-HCO, retard the rate as expected. The substituent effect was studied by plotting the log of the relative rate constants versus the sigma constants (Fig. 30).

As it is known, the σ and σ^- constants were derived from the acidic ionization of the substituted benzoic acids and the substituted phenols. The σ^- constants are required when there is a direct conjugation between the reaction site and the substituent. However, in the case of the thiophenols, the special σ values for the electron attracting groups, such as p-NO₂, p-HCO and p-CH₃CO, are required in order to get a good correlation, since the SH group does not resonate as strongly with the benzene ring, although the SH group is electronically closely related to the OH group.

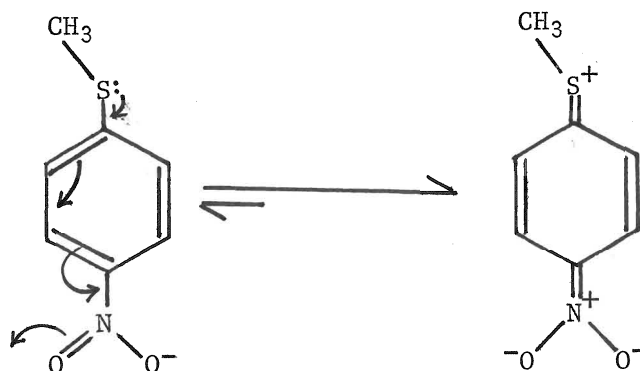
Bordwell et al. (67) and Schwarzenbach et al. (68-70) have derived the σ^* constants of 1.081 and 0.717 for the p-NO₂ and the p-CH₃CO groups respectively from the ionization of thiophenols in 48% ethanol. These values are approximately intermediary between the σ and the σ^- constants. No work was done to determine the σ^* value for the HCO group. The average value of the σ and the σ^- was calculated to be the σ^* (0.671) constant for the p-HCO,

because of the similarity between the calculated and the observed values of σ^* for p-NO₂ and p-CH₃CO.

These special sigma values σ^* were used in order to get a good correlation, because of the similar electronic character of the sulfides.

The reaction constants (ρ) were calculated by using the third order rate constants of the oxidation of the phenylmethyl sulfide, p-methoxy, p-methyl, p-nitro, p-acetyl and p-formyl (in σ^* case) phenylmethyl sulfides. The ρ values are found to be -2.082, -1.57 and -1.374 when σ ,^a σ^* and σ^{-a} constants are used respectively. The 4-methylthiobenzaldehyde showed a significant positive and negative deviation when σ and σ^- values were used, but a good correlation was obtained when the σ^* constant was used.

The correlation coefficients with the σ , σ^* , and the σ^- constants are similar: 0.99536, 0.99600, and 0.99544, respectively. However, the use of the σ^* constants seems to be reasonable due to the similar electronic structure of the sulfides and the thiols. However, these correlation constants and the ρ values -2.082, -1.57 and -1.374 indicate an electron rich transition state in the rate determining step. Because of the through conjugation, the equilibria are driven to the right by the contribution of the structure below.



^a taken from Ref. 71.

Table 11. Activation energies for the oxidation of phenylmethyl sulfide and p-methoxy-, p-methyl-, p-nitro- and p-acetyl-phenylmethyl sulfides.

Sulfide	Catalyst	Radiation by	k_3 at 35°C $M^{-2}min^{-1}$	Temperature Range (°C)	E_a kcal mol^{-1}	$\ln A$
ϕSMe^1	$MoO_2(acac)_2$	--	2279	27-45	18,365	37.61
ϕSMe^2	"	UV	3843	25-35	17,199	33.36
ϕSMe^3	$Mo(CO)_6$	UV	3582	19-40	12,464	28.54
$CH_3O\phi SMe^4$	$MoO_2(acac)_2$	--	6396*	15-35	14,734	32.84
$CH_3\phi SMe^5$	"	--	4551	15-35	16,417	35.22
$NO_2\phi SMe^6$	"	--	38**	60-76	24,877	44.29
$CH_3C(=O)\phi SMe^7$	"	--	230**	60-70	21,346	40.31

* Average value of runs 41, 62, 63

** Calculated from Arrhenius plot

¹ Data from Table 7, Figure 23

² Data from Table 3, Figure 28

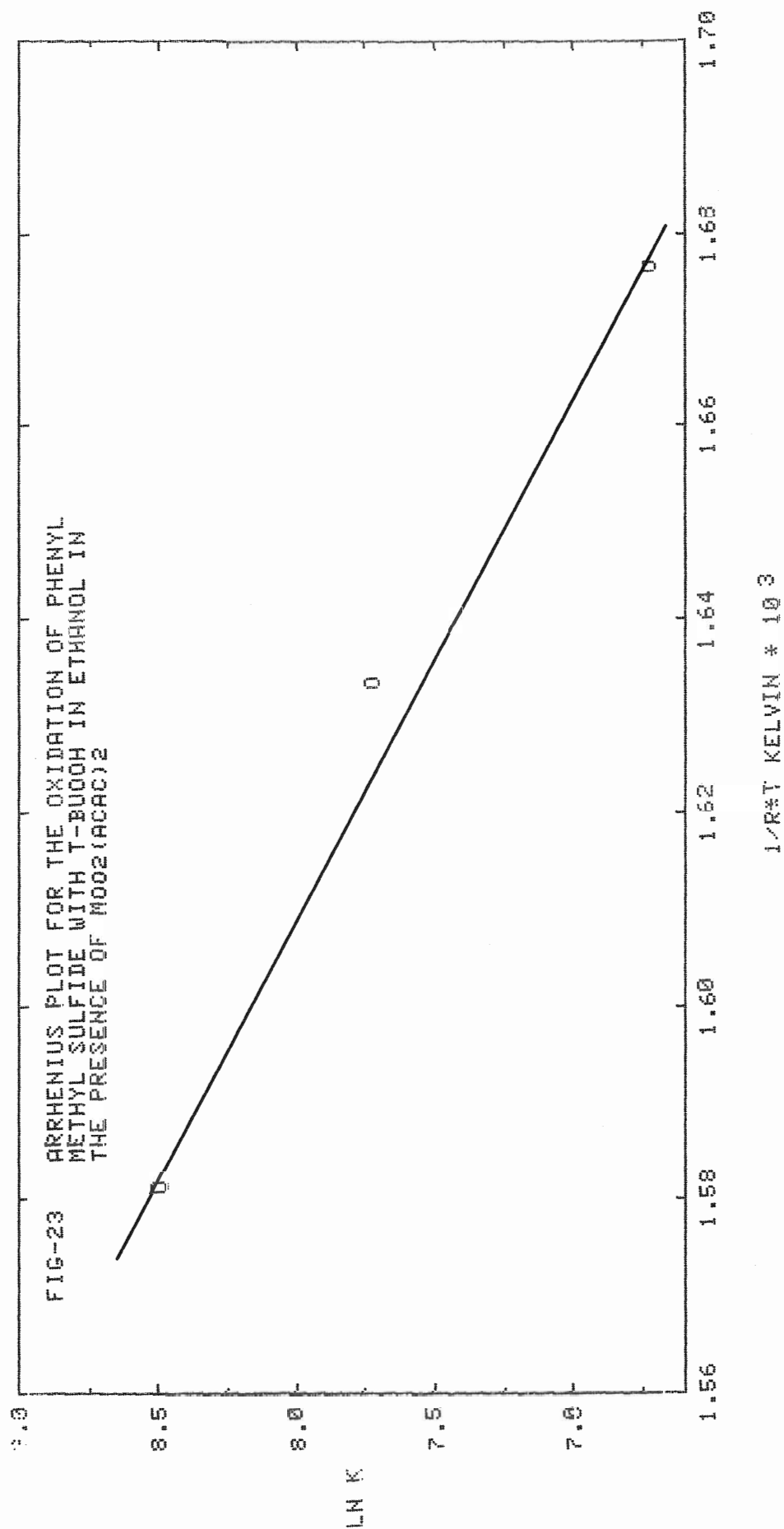
³ Data from Table 3, Figure 29

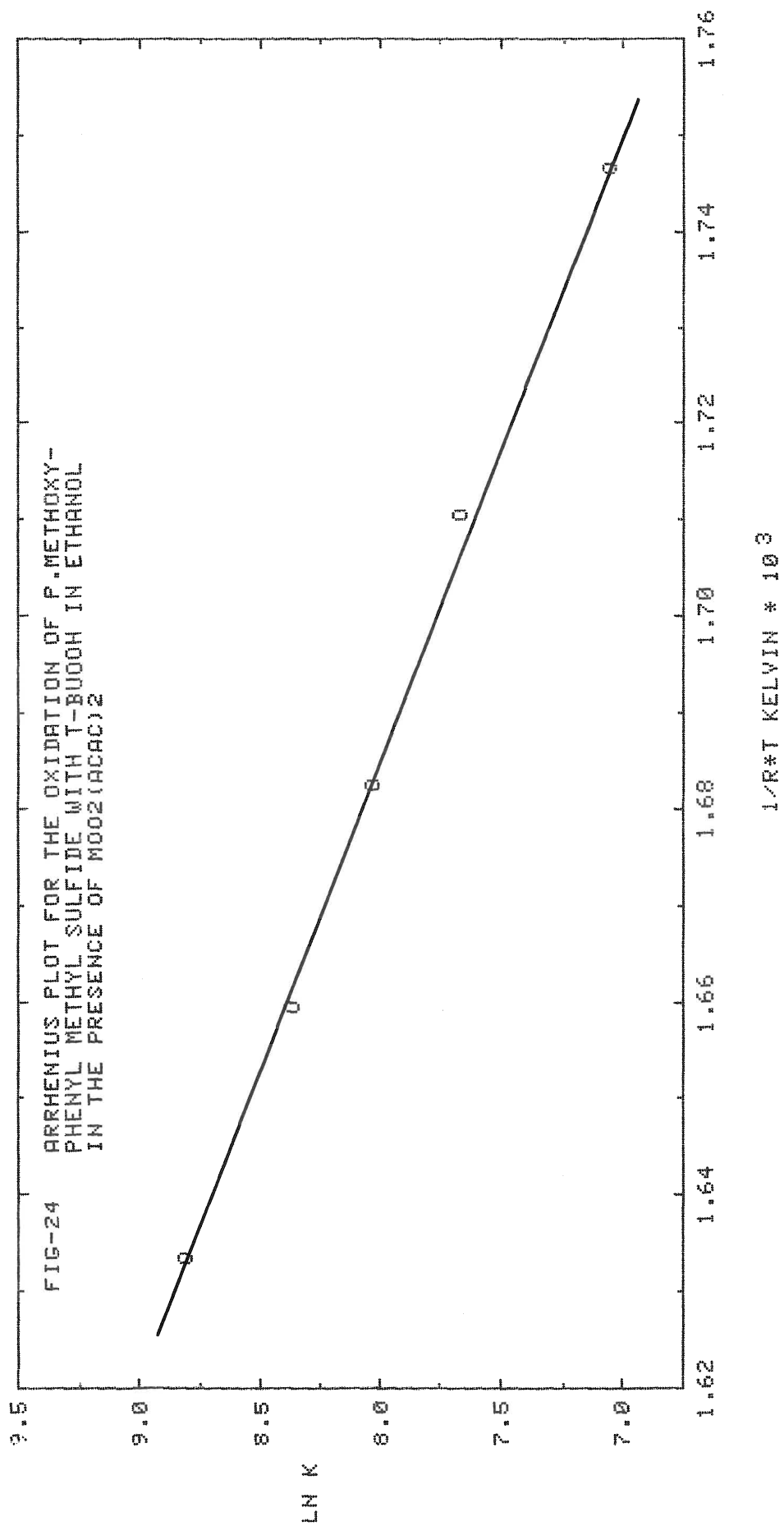
⁴ Data from Table 8, Figure 24

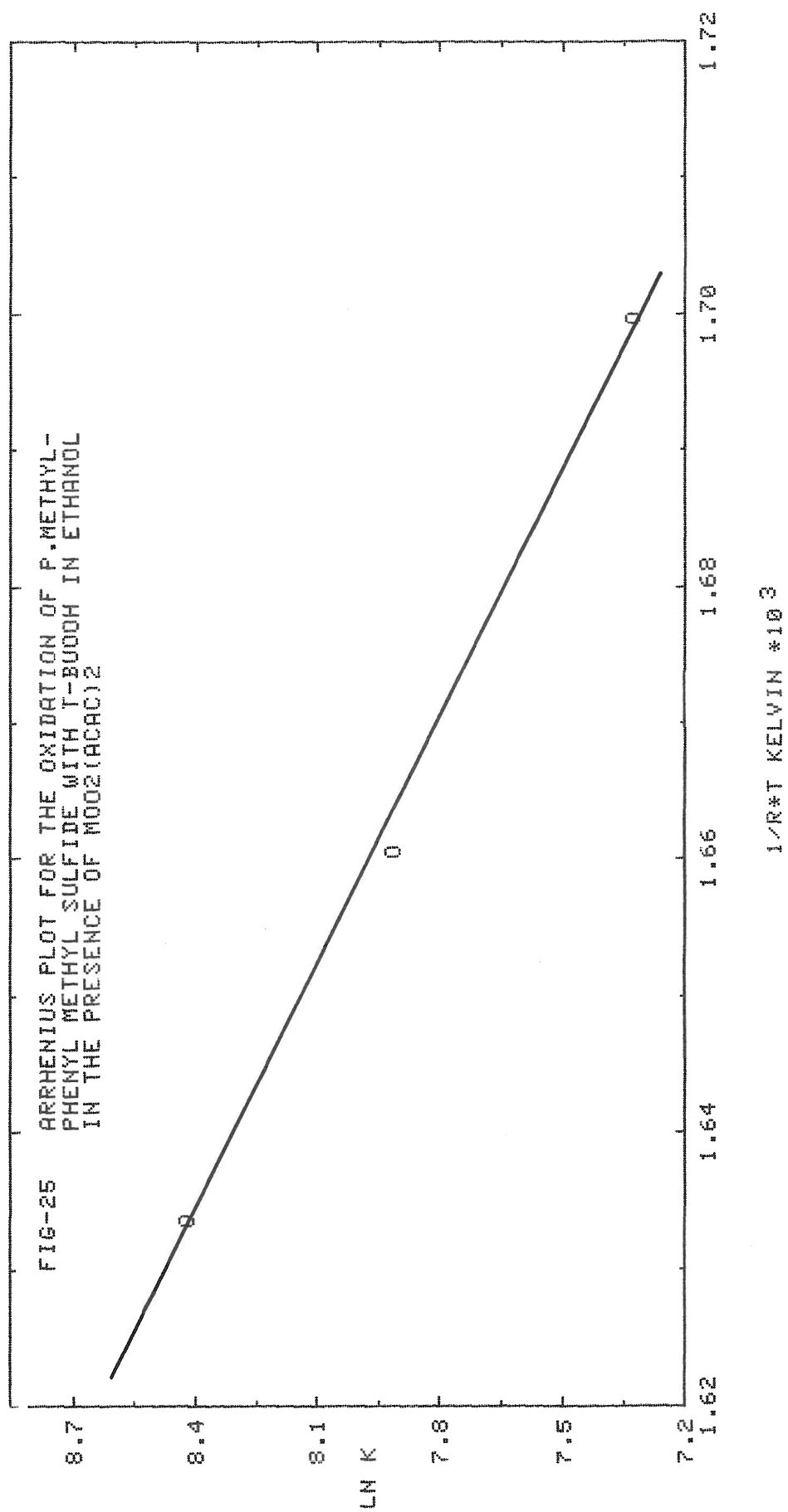
⁵ Data from Table 9, Figure 25

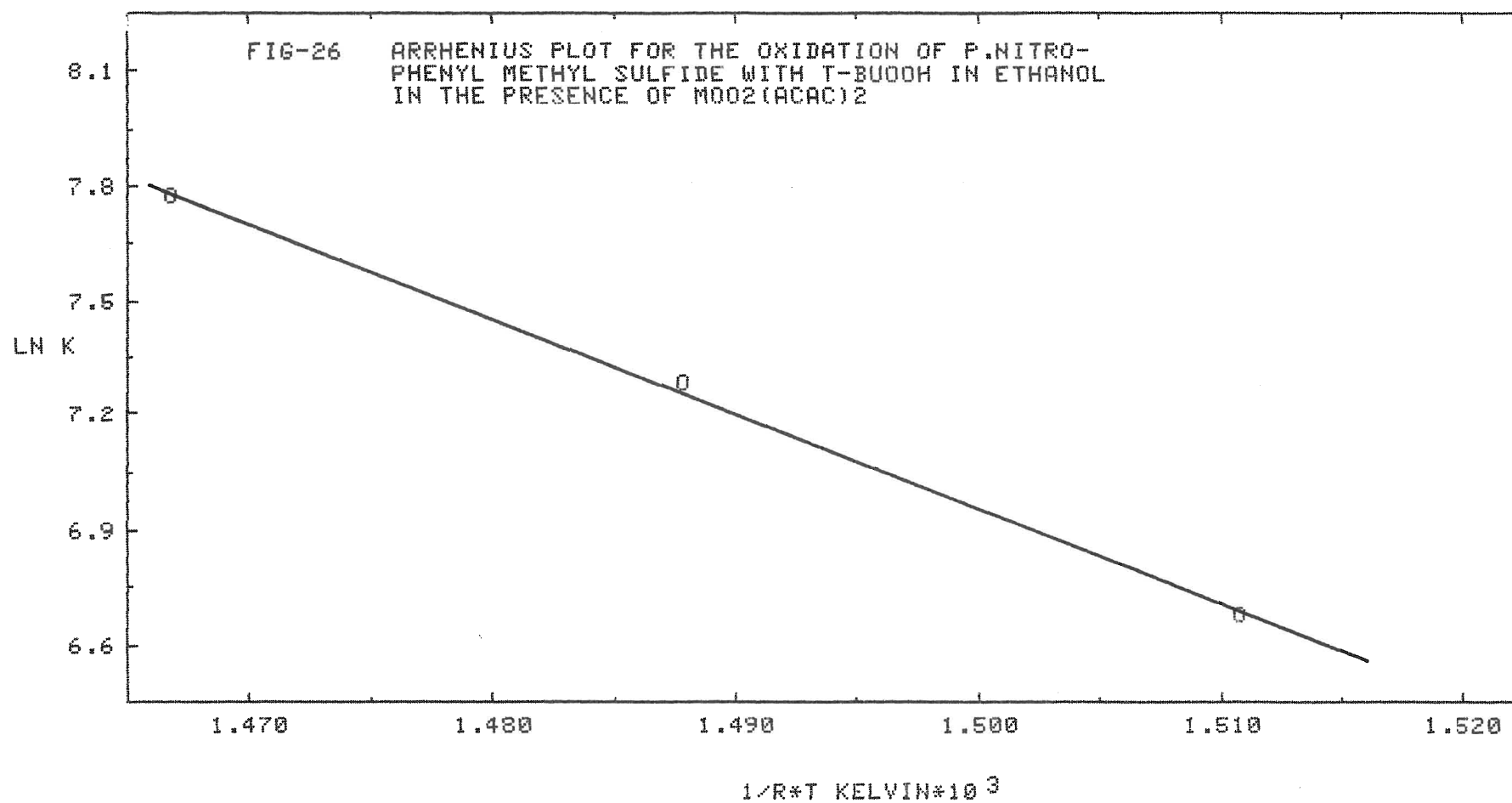
⁶ Data from Table 10, Figure 26

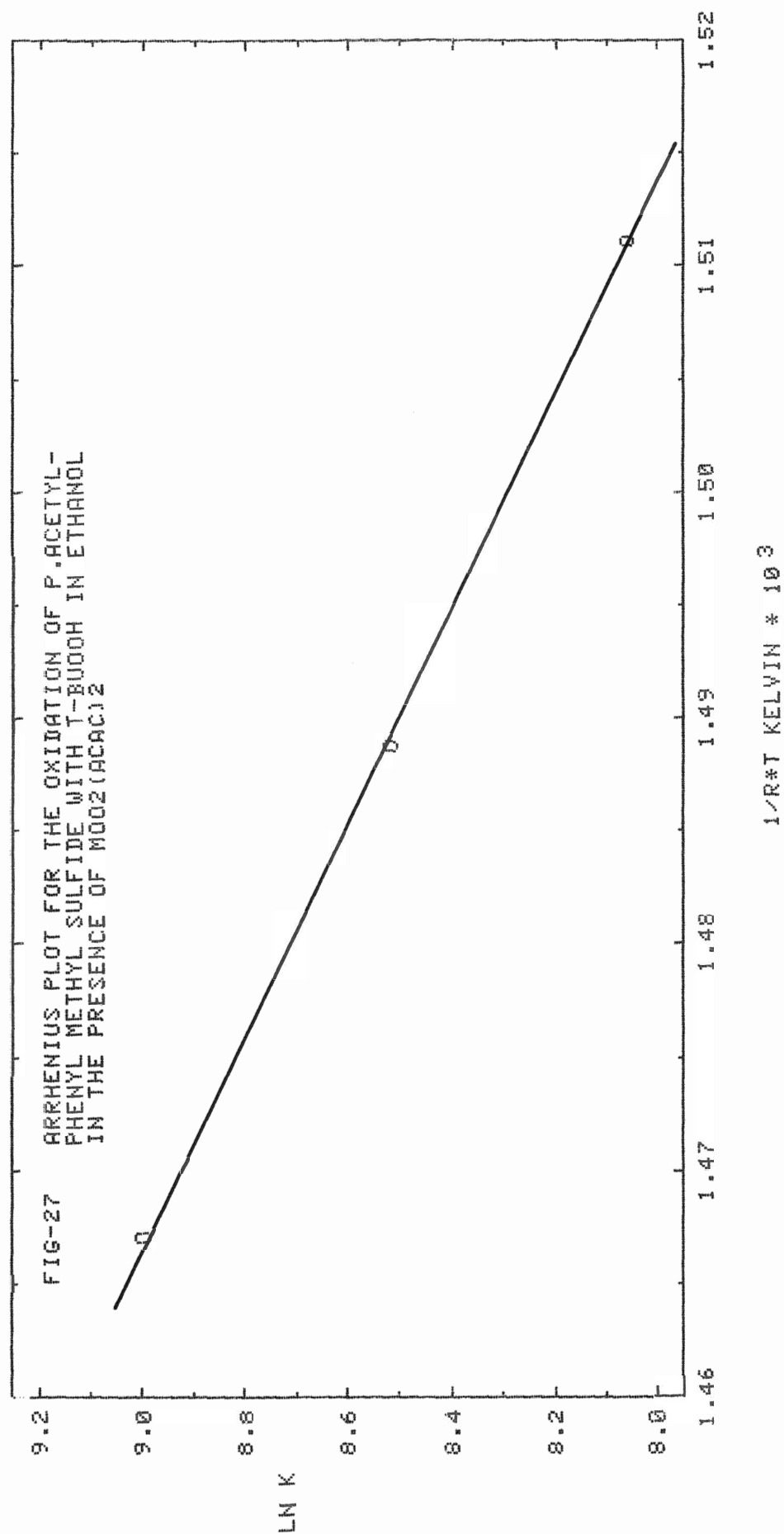
⁷ Data from Table 10, Figure 27

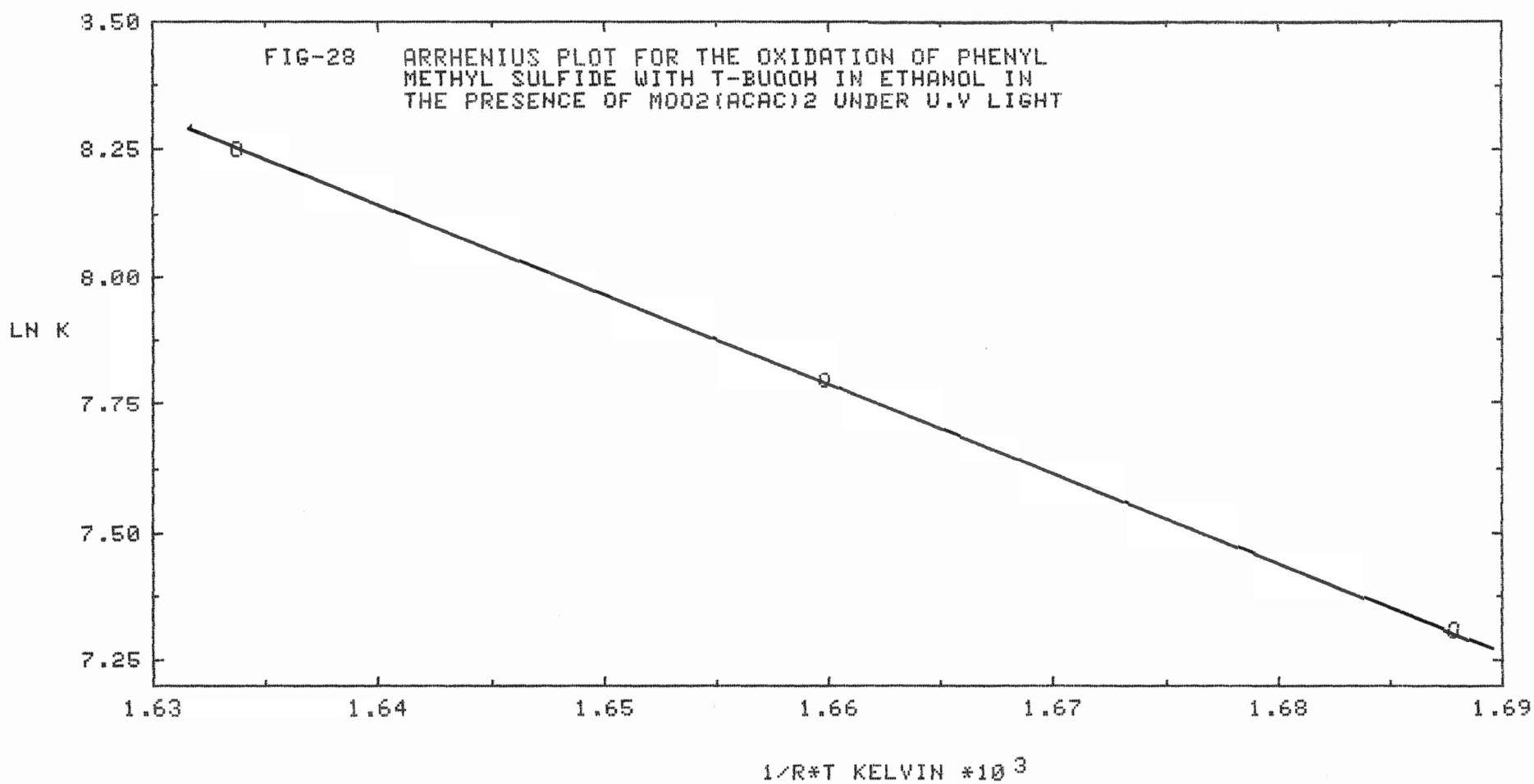


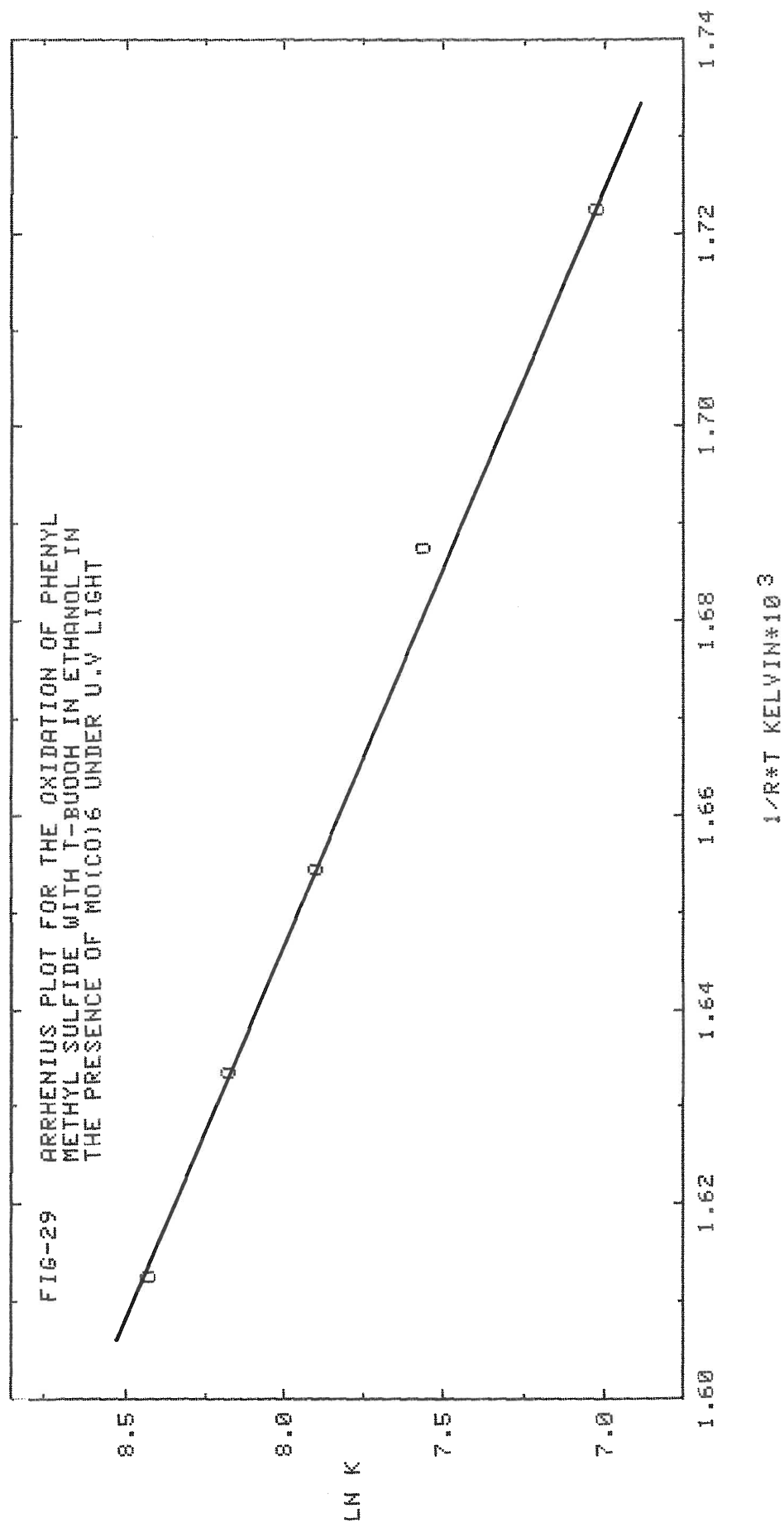


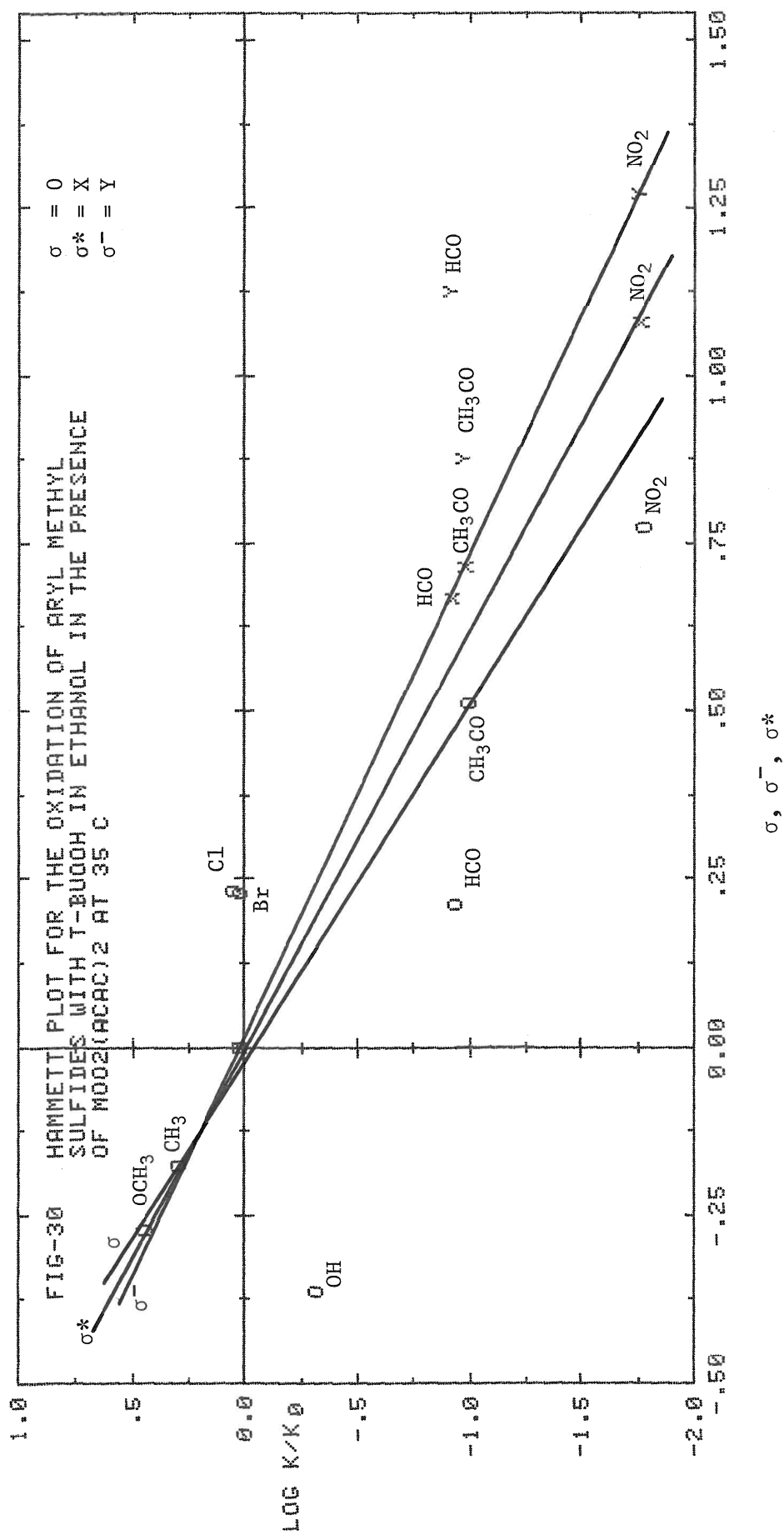












The ρ values are larger than those found in the acid-catalyzed oxidation of the arylmethyl sulfides by hydrogen peroxide in ethanol ($\rho = -1.13$ (37)). Also, the ρ values are of the same order as found by Hiatt and Howe (14,36) for the $\text{VO}(\text{acac})_2$ -catalyzed oxidation of aniline by $t\text{-BuO}_2\text{H}$ in benzene-chloroform at 60°C ($\rho = -1.63$), and for molybdenum-catalyzed epoxidation of the substituted styrenes in benzene at 60°C ($\rho = -1.37$). Modena et al. (41) had shown that the effect of substituents is smaller than expected in the $\text{VO}(\text{acac})_2$ -catalyzed oxidation of arylmethyl sulfides by hydrogen peroxide ($\rho = -0.5$). Their results seem to be inconsistent with the above results.

The behaviour of the *p*-hydroxyphenylmethyl sulfide was surprising because it reacts more slowly than phenylmethyl sulfide and the rate of reaction decreases gradually as the concentrations of $t\text{-BuO}_2\text{H}$ decreases (Fig. 19). The abnormal reactivity of this compound can be ascribed to the complex formation with the catalyst through the OH group. The decrease in rate clearly shows that *p*-hydroxyphenylmethyl sulfide can compete with $t\text{-BuO}_2\text{H}$ (in low concentration) in complexing with the catalyst. The rate of this reaction was calculated from the first three points on the second order rate plot to obtain an approximate value.

The effect of halogens is also surprising. In agreement with Köseoğlu (46), *p*-Cl and *p*-Br phenylmethyl sulfides gave faster reactions than phenylmethyl sulfide. In the $\text{VO}(\text{acac})_2$ catalyzed oxidation of *p*-chlorophenylmethyl sulfide by hydrogen peroxide, however, the rates were found to be less than with phenylmethyl sulfide (41). It is difficult to compare these two

systems, since different catalysts and oxidants were used. However, Modena et al. (40) had shown that chloride ion acts as a co-catalyst in the oxidation of organic sulfides by $t\text{-BuO}_2\text{H}$ in the presence of $\text{VOCl}_3\text{-EtO}^-$,* $\text{VO}(\text{acac})_2$, $\text{VO}(\text{OEt})_3$. Second order rate constants for the oxidation of $(n\text{-Bu})_2\text{S}$ in ethanol at 25°C were found to be 15.4×10^{-3} , 2.1×10^{-3} , and 0.5×10^{-3} , respectively in the presence of the above catalysts. The explanation was based on the formation of the same triethyl vanadate esters for each catalyst in the reaction. The higher reactivity of $\text{VOCl}_3\text{-EtO}^-$ catalyst was linked to the chloride ion in solution.

Furthermore, initial addition of $(n\text{-Bu})_4\text{N}^+\text{Cl}^-$ salt to the reaction in the $\text{VO}(\text{acac})_2$ -catalyzed oxidation of either $(n\text{-Bu})_2\text{S}$ or $p\text{-chlorophenylmethyl}$ sulfide with $t\text{-BuO}_2\text{H}$ increased the reaction rate. Observations showed that the rate increased gradually with increasing concentration of salt. The addition of $(n\text{-Bu})_4\text{N}^+\text{ClO}_4^-$ showed no catalytic effect.

The greater reactivity of $p\text{-chlorophenylmethyl}$ sulfide can be assumed to be similar to that observed by Modena (40). The chlorine-containing catalytically active species which forms between $p\text{-chlorophenylmethyl}$ sulfide and molybdenum catalyst via the chlorine atom gives a fast reaction for this compound, as does $p\text{-bromophenylmethyl}$ sulfide. Further studies, however, are needed to validate this assumption.

* Triethyl vanadate ester $\text{VO}(\text{OEt})_3$ was prepared from VOCl_3 , which was added to dry ethanol; excess acid was neutralized with sodium ethoxide.

$\text{VOCl}_3\text{-EtO}^-$ indicates that the above solution was used as a catalyst solution.

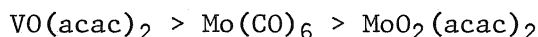
V. The decomposition of t-butyl hydroperoxide in the presence of TM complexes

In the absence of sulfide, no decomposition of t-BuO₂H was observed in the presence of 4.0×10^{-3} M of Mo(CO)₆ in ethanol at 35°C under UV radiation in 2.5 hours. The decompositions of t-BuO₂H were observed, however, at high concentrations of catalysts. The decompositions of t-BuO₂H (followed by iodometric titration, in the presence of the saturated solutions of Mo(CO)₆, MoO₂(acac)₂ and VO(acac)₂ in ethanol) were first order (Figs. 31-33). The results of the kinetic measurements are given in Table 12.

Relative rates are calculated by using Equation 57. First order dependency on the catalyst was assumed.

$$\text{Rate} = k_1[\text{HP}] \qquad k_1 = k_2[\text{cat}] \qquad (57)$$

The relative decomposition rates of t-BuO₂H in the presence of metal complexes are in the order



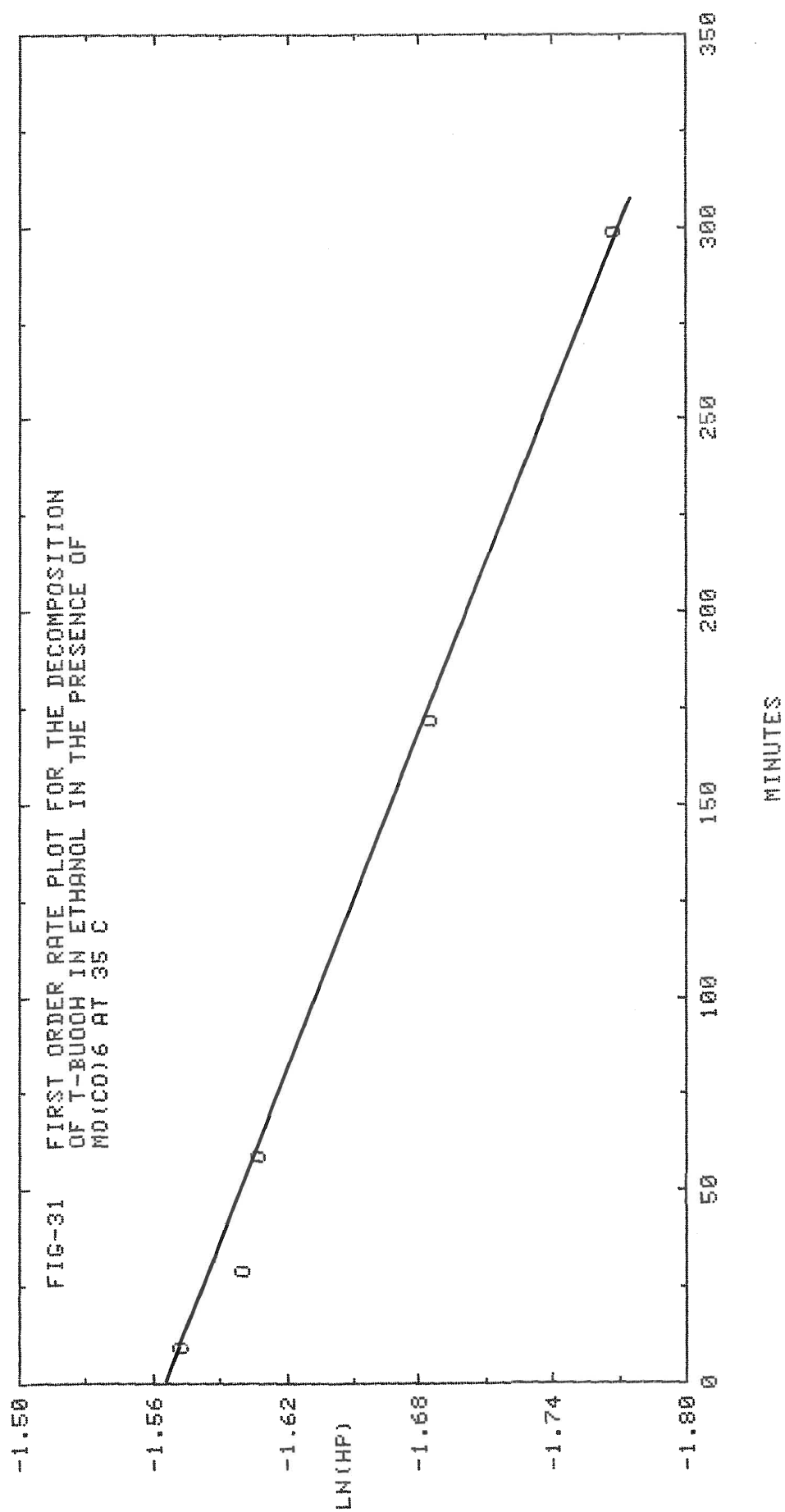
The products of decomposition were not analyzed as they were not needed.

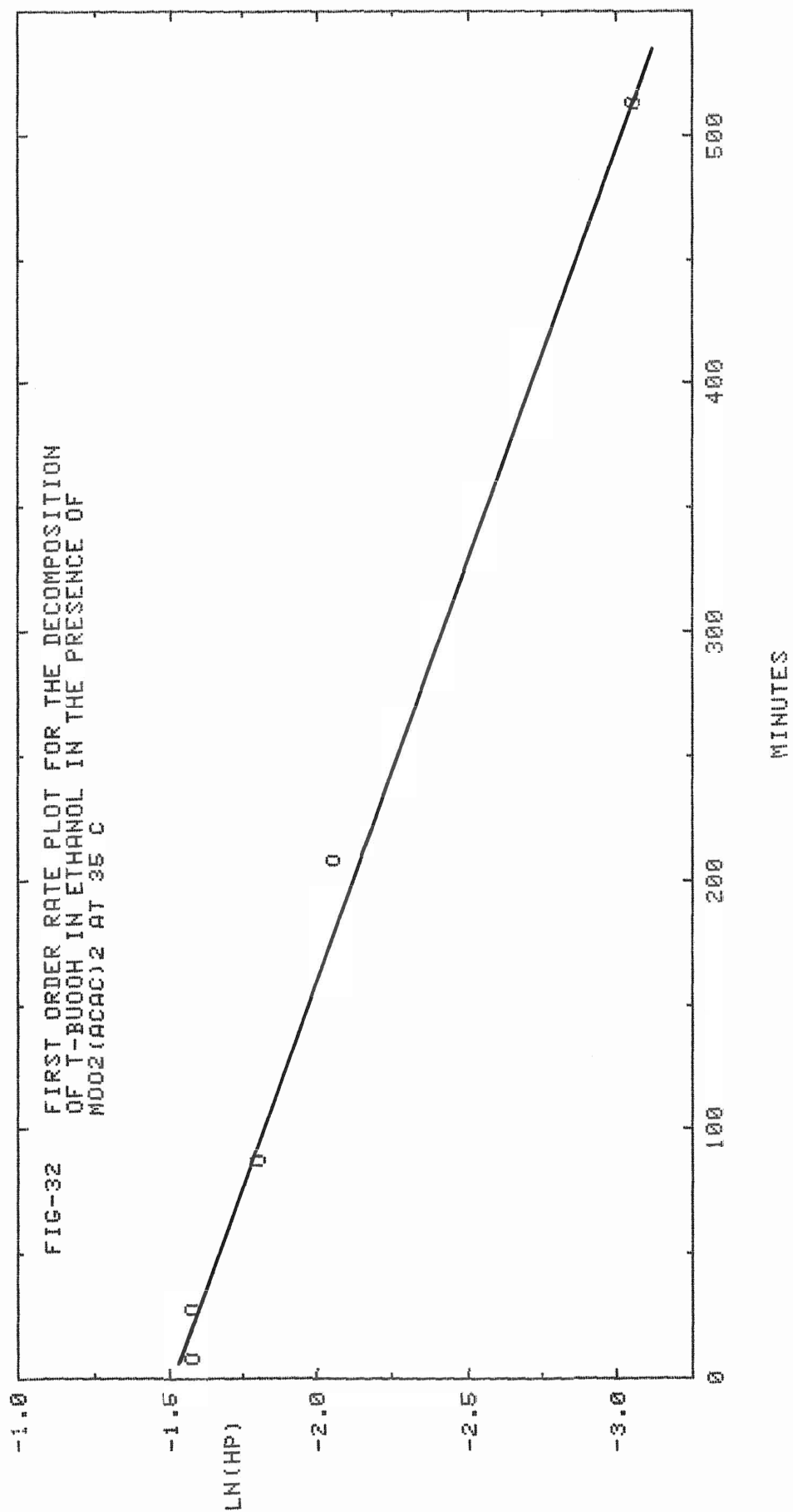
The results clearly show that there is no significant decomposition of t-BuO₂H under the reaction conditions; although the decomposition of t-BuO₂H was observed at high concentration of catalyst, the rates were very small compared to those for the oxidation reactions.

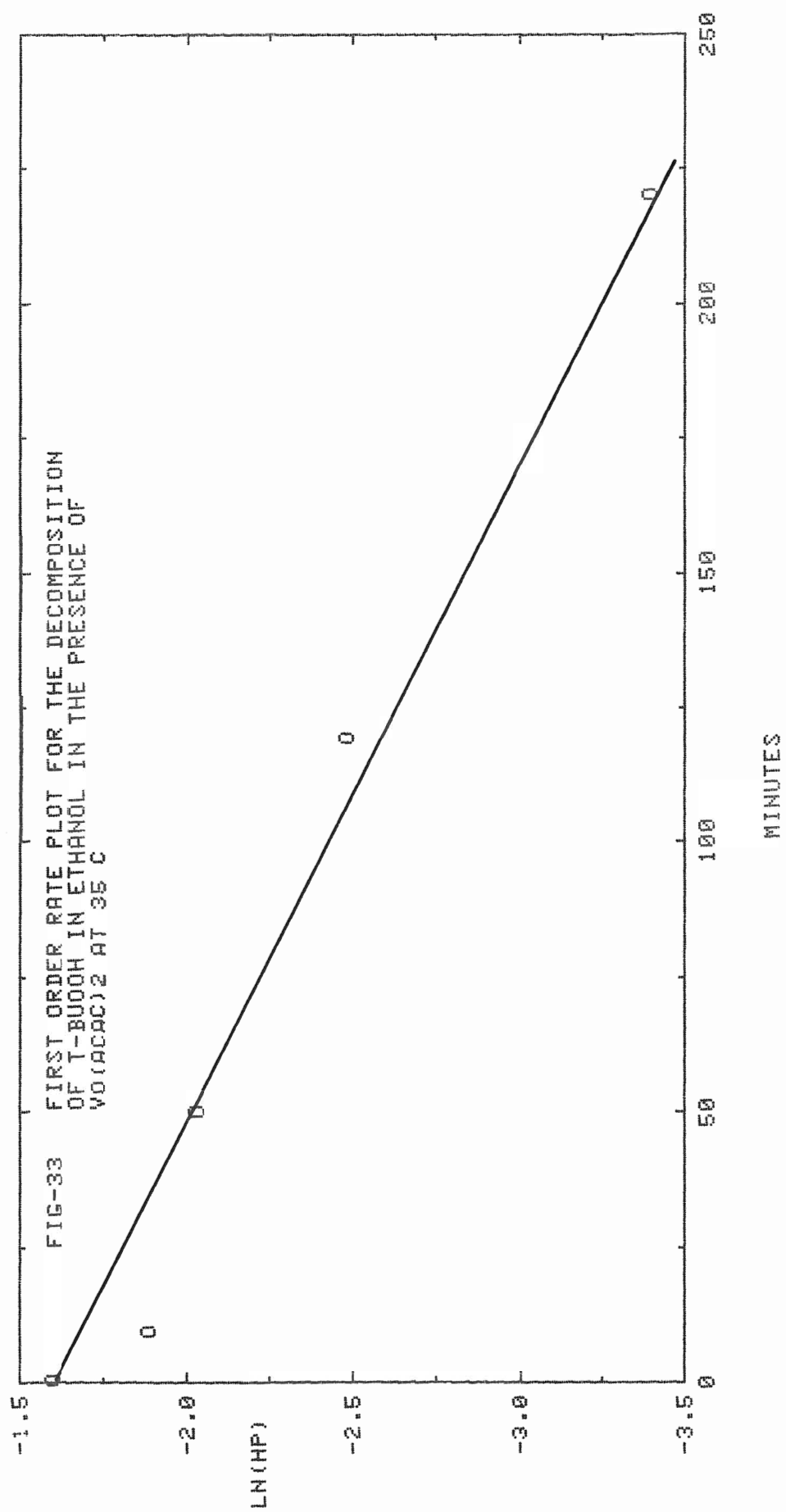
Table 12. Rates of the decomposition of t-butylhydroperoxide in ethanol at 35°C

Run Number	[t-BuO ₂ H]	Catalyst	[Cat] x 10 ²	Radiation by	k ₁ x 10 ³ M ⁻¹ min ⁻¹	k ₂ x 10 ² M ⁻¹ min ⁻¹
74	0.2068	Mo(CO) ₆	2.084	--	0.6539	3.137
79	0.2051	VO(acac) ₂	9.340	--	7.558	8.092
80	0.2069	MoO ₂ (acac) ₂	13.51	--	2.947	2.181
146	0.2050	Mo(CO) ₆	0.4083	UV	No decomposition in 2.5 hours	

^a under air atmosphere







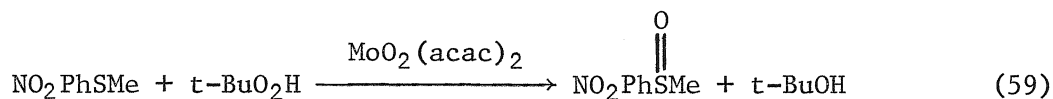
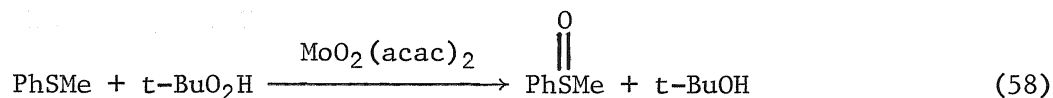
VI. Competitive reactions of p-methoxy, p-nitro and unsubstituted phenylmethyl sulfides

In hope of observing the effect of sulfide as a co-catalyst, p-nitro-phenylmethyl sulfide with phenylmethyldisulfide, and with p-methoxyphenylmethyl sulfide were oxidized together by t-BuO₂H in the presence of MoO₂(acac)₂ at 40°C.

The aim of these reactions was to see the effect of either phenylmethyl sulfide or p-methoxyphenylmethyl sulfide in the oxidation of p-nitrophenylmethyl sulfide. If the sulfide acts as a co-catalyst, it would mean that it plays an important role in determining the structure of the catalyst, and the oxidation rate of p-nitrophenylmethyl sulfide will be higher than when it is reacted alone.

The reactions were followed by monitoring the disappearance of the sulfides and the formation of the sulfoxides by UV analysis (Figs. 34-35).

The kinetic treatment of this data is very simple; by assuming that both reactions follow second order kinetics (Eqs. 58, 59) as is the case when they are reacted alone.



The rate Equations (60, 61) for the disappearance of both sulfides may be written as:

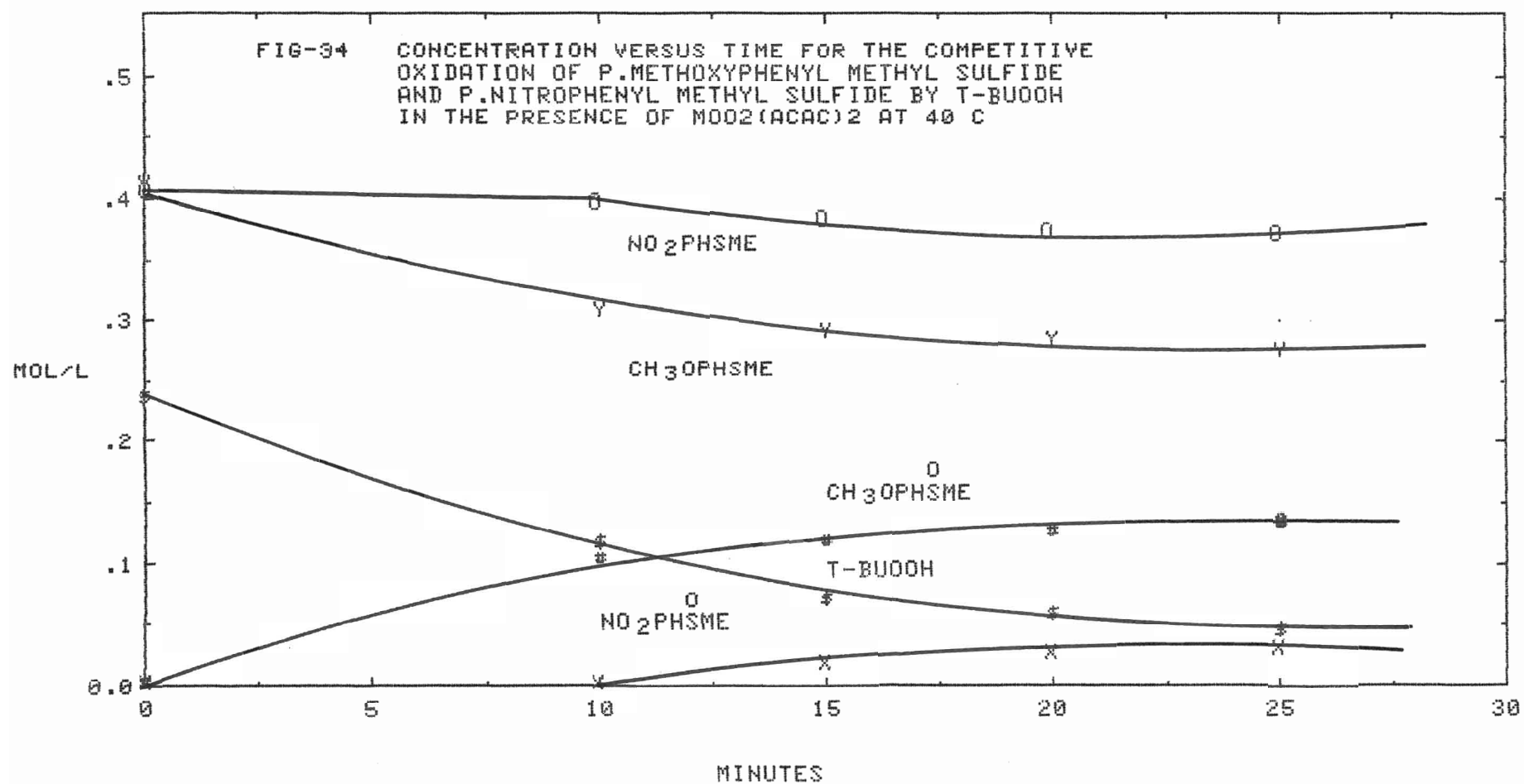
Table 13. The relative rate constants for the oxidation of phenylmethyl sulfide and p-nitrophenylmethyl sulfide, and p-methoxyphenylmethyl sulfoxide and p-nitrophenylmethyl sulfide by t-BuO₂H in the presence of MoO₂(acac)₂.

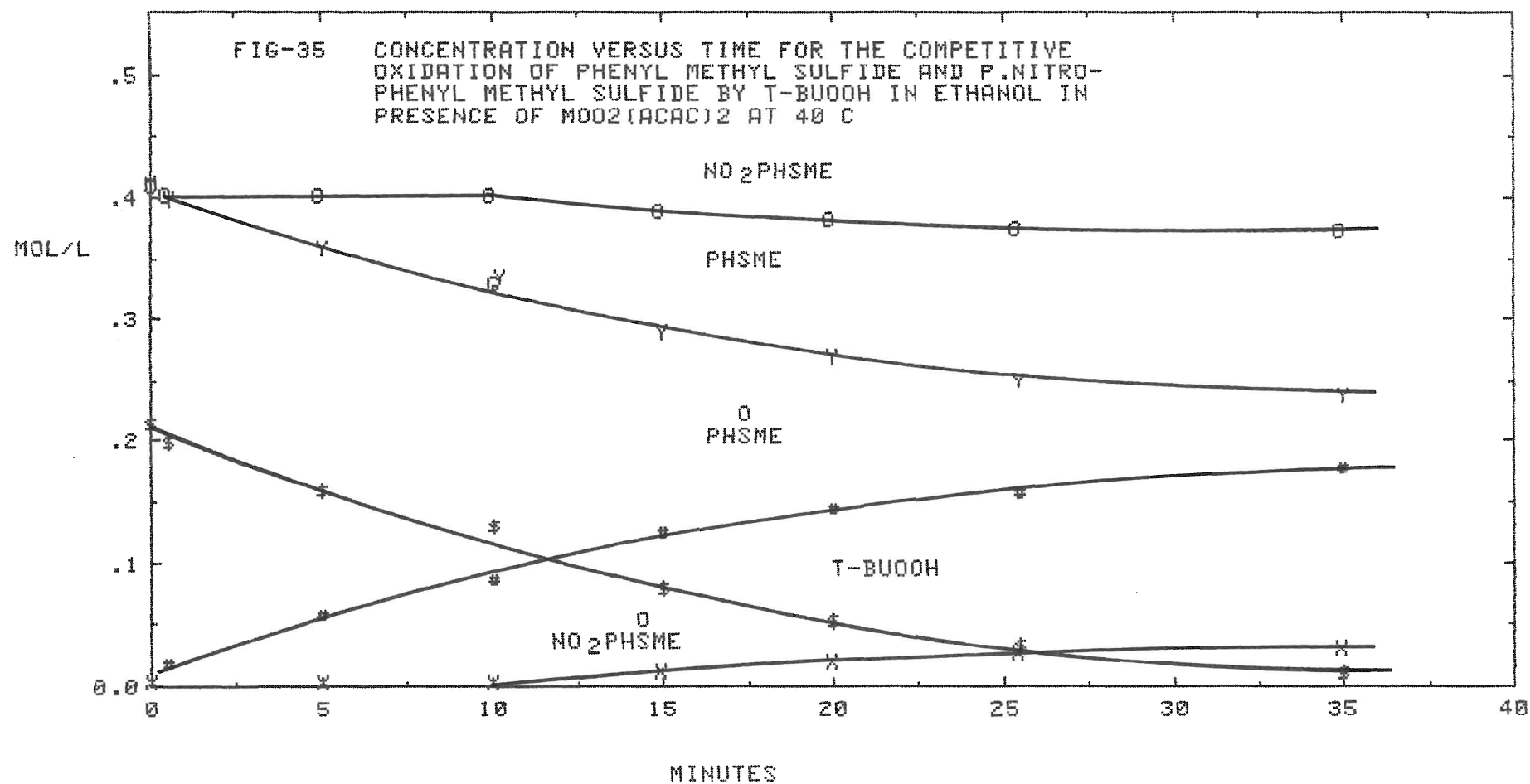
Substrate	k_3/k'_3 ^{a,c}	k_3/k'_3 ^{b,c}
PhSMe NO ₂ PhSMe	3.923	44.06
CH ₃ OPhSMe NO ₂ PhSMe	1.249	128.33

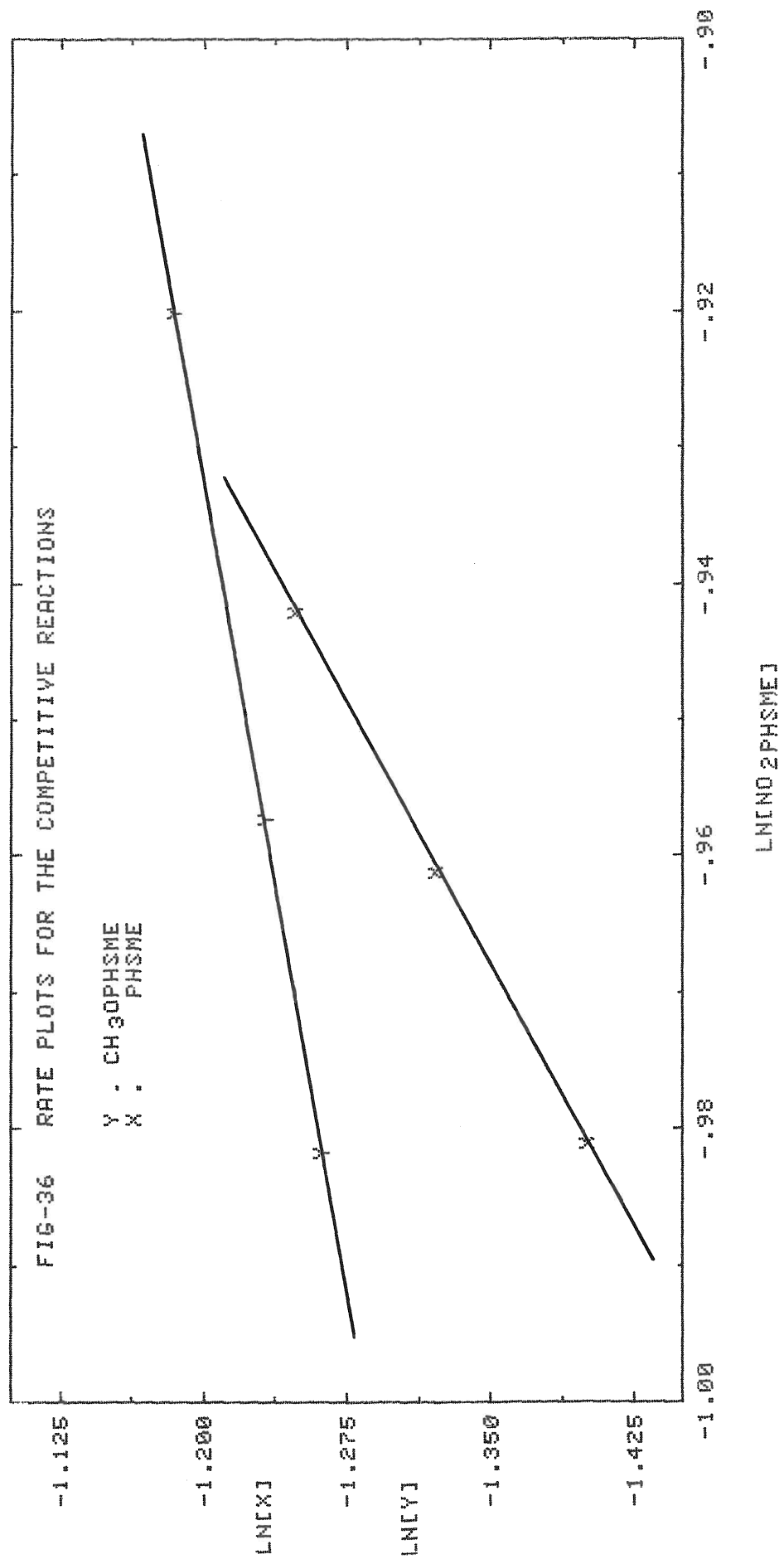
^a From the competitive reaction

^b From the individual reactions

^c At 40°C, in ethanol, and under nitrogen atmosphere







$$\frac{-\partial [\text{PhSMe}]}{\partial t} = k_2 [\text{PhSMe}] [\text{t-BuO}_2\text{H}] \quad k_2 = k_3 [\text{cat}] \quad (60)$$

$$\frac{-\partial [\text{NO}_2\text{PhSMe}]}{\partial t} = k_2' [\text{NO}_2\text{PhSMe}] [\text{t-BuO}_2\text{H}] \quad k_2' = k_3' [\text{cat}] \quad (61)$$

Division of Equation 60 by Equation 61 and integration yields Equation 62.

$$\ln [\text{PhSMe}] = \frac{k_2}{k_2'} \ln [\text{NO}_2\text{PhSMe}] \quad (62)$$

The logarithm of the concentration of p-nitrophenylmethyl sulfide was plotted against the logarithm of the concentration of phenylmethyl sulfide and relative rate constants were obtained from the slope of this line (Fig. 36). The relative rate constants obtained from the competition reactions and the individual reactions are listed in Table 13.

The values of k_3/k_3' for the competition reactions between phenylmethyl sulfide and p-methoxyphenylmethyl sulfide could not be determined from the complicated UV data.

The value of $k_3(\text{CH}_3\text{O})/k_3'(\text{NO}_2)$ is higher when the sulfides are reacted together than when the sulfides are reacted individually. It is obvious that the p-nitrophenylmethyl sulfide is more reactive in the presence of p-methoxyphenylmethyl sulfide and phenylmethyl sulfide than when it is reacted alone. These results clearly indicate that both phenylmethyl sulfide and p-methoxyphenylmethyl sulfide behave as a co-catalyst in the oxidation of p-nitrophenylmethyl sulfide and their reactivities increase with the electron donating groups on the co-catalyst.

VII. The solvent effect on the oxidation of phenylmethyl sulfide

In addition to ethanol, cyclohexane, benzene and mesitylene were used as solvents in the Mo(CO)_6 - and $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation of phenylmethyl sulfide by $t\text{-BuO}_2\text{H}$ at 35°C , either under normal light conditions or under UV radiation. Cyclohexane could not be used in the $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation because of the poor solubility of the catalyst.

All the solvents except ethanol were chosen at the same polarity and according to their π donating ability. The assumption was to observe the complexation of the solvents with the catalyst under UV radiation.

The third order rate constants (Table 14) show that the behaviour of both catalysts depends upon both the solvent and the light conditions. The results obtained in the Mo(CO)_6 -catalyzed oxidations under normal light conditions are not reliable due to lack of reproducibility of these systems, although straightforward reactions were observed. It is therefore very difficult to describe the effect of solvents in these systems.

The solvent effect on the oxidation reactions under UV radiation, however, can be explained by two factors:

- (i) the formation of solvent-molybdenum complex, and
- (ii) involvement in the transition state to assist the heterolysis of the peroxide O-O bond.

It is known that reactions are promoted by solvent capable of hydrogen bonding to $t\text{-BuO}_2\text{H}$ (72) (or in its absence by a second hydroperoxide) as shown in Equation 50.

Table 14. The oxidation of phenylmethyl sulfide with t-BuO₂H in the presence of Mo(CO)₆ and MoO₂(acac)₂ in various solvents.^a

Run Number	[PhSMe]	[t-BuO ₂ H]	Catalyst	[cat] x 10 ⁵	Light conditions	Solvent	k ₂ x 10 ² M ⁻¹ min ⁻¹	k ₃ M ⁻² min ⁻¹
116	1.017	0.209	Mo(CO) ₆	3.252	UV	benzene	14.37	4421
117	1.025	0.209	Mo(CO) ₆	2.741	UV	c-hexane	8.480	3094
157	1.020	0.205	Mo(CO) ₆	2.821	UV	ethanol	10.11	3582
120	1.022	0.211	Mo(CO) ₆	2.655	UV	mesitylene	12.08	4526
123	1.023	0.211	Mo(CO) ₆	2.682	normal	benzene	0.05700	21.27
126	1.020	0.211	Mo(CO) ₆	2.613	normal	c-hexane	0.1221	46.74
125	1.021	0.206	Mo(CO) ₆	2.765	normal	ethanol	0.03570	12.91
121	1.016	0.211	Mo(CO) ₆	2.821	normal	mesitylene	0.1470	52.15
127	1.015	0.208	MoO ₂ (acac) ₂	2.607	UV	benzene	4.109	1576
129	1.024	0.205	MoO ₂ (acac) ₂	2.653	UV	mesitylene	3.477	1307
96	1.007	0.206	MoO ₂ (acac) ₂	2.667	UV	ethanol	10.23	3843
128	1.017	0.211	MoO ₂ (acac) ₂	2.883	normal	benzene	2.505	869.0
130	1.024	0.210	MoO ₂ (acac) ₂	2.530	normal	mesitylene	3.457	1366
53	1.055	0.206	MoO ₂ (acac) ₂	2.407	normal	ethanol	5.490	2279

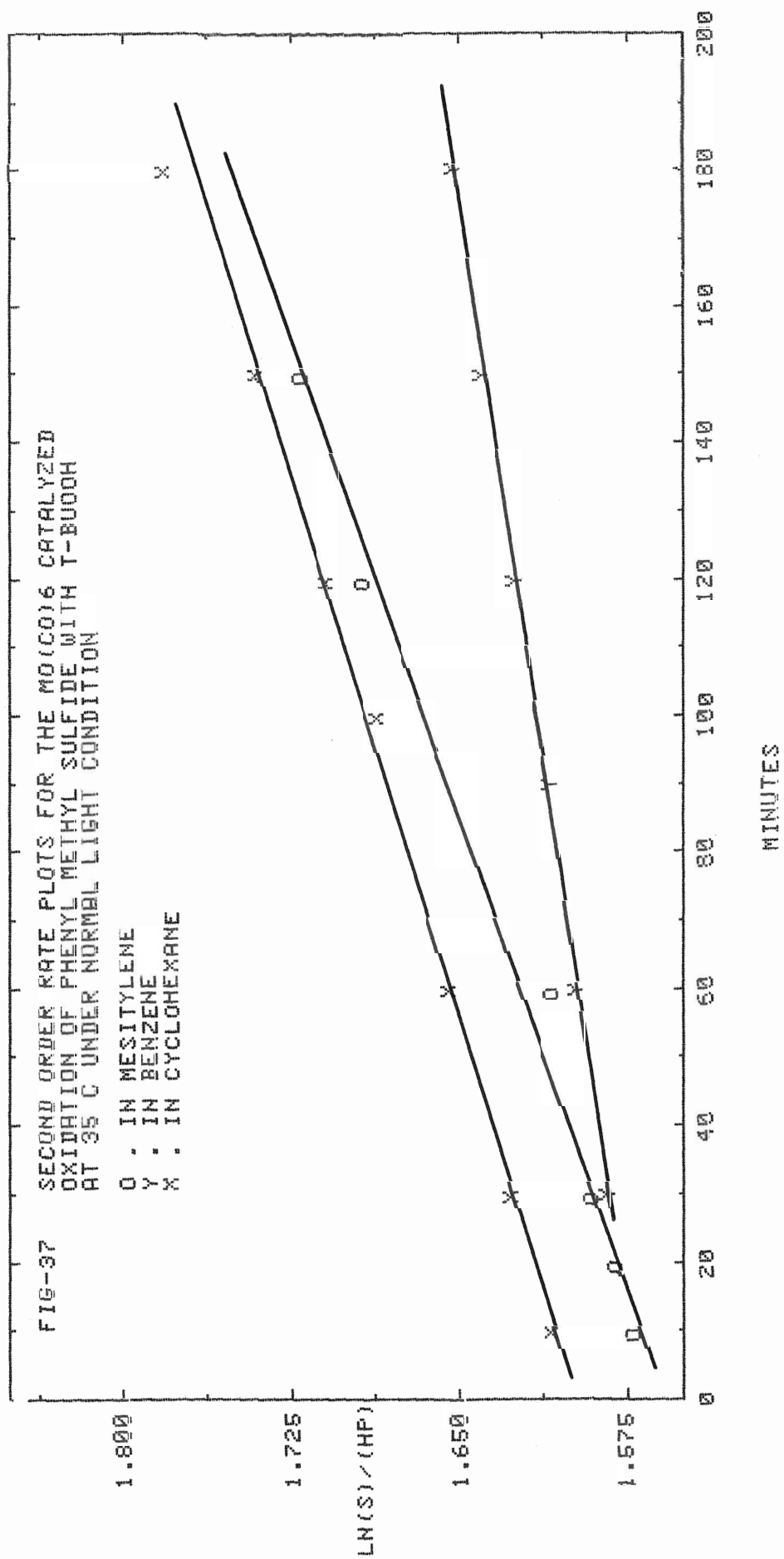
^a at 35°C under nitrogen atmosphere

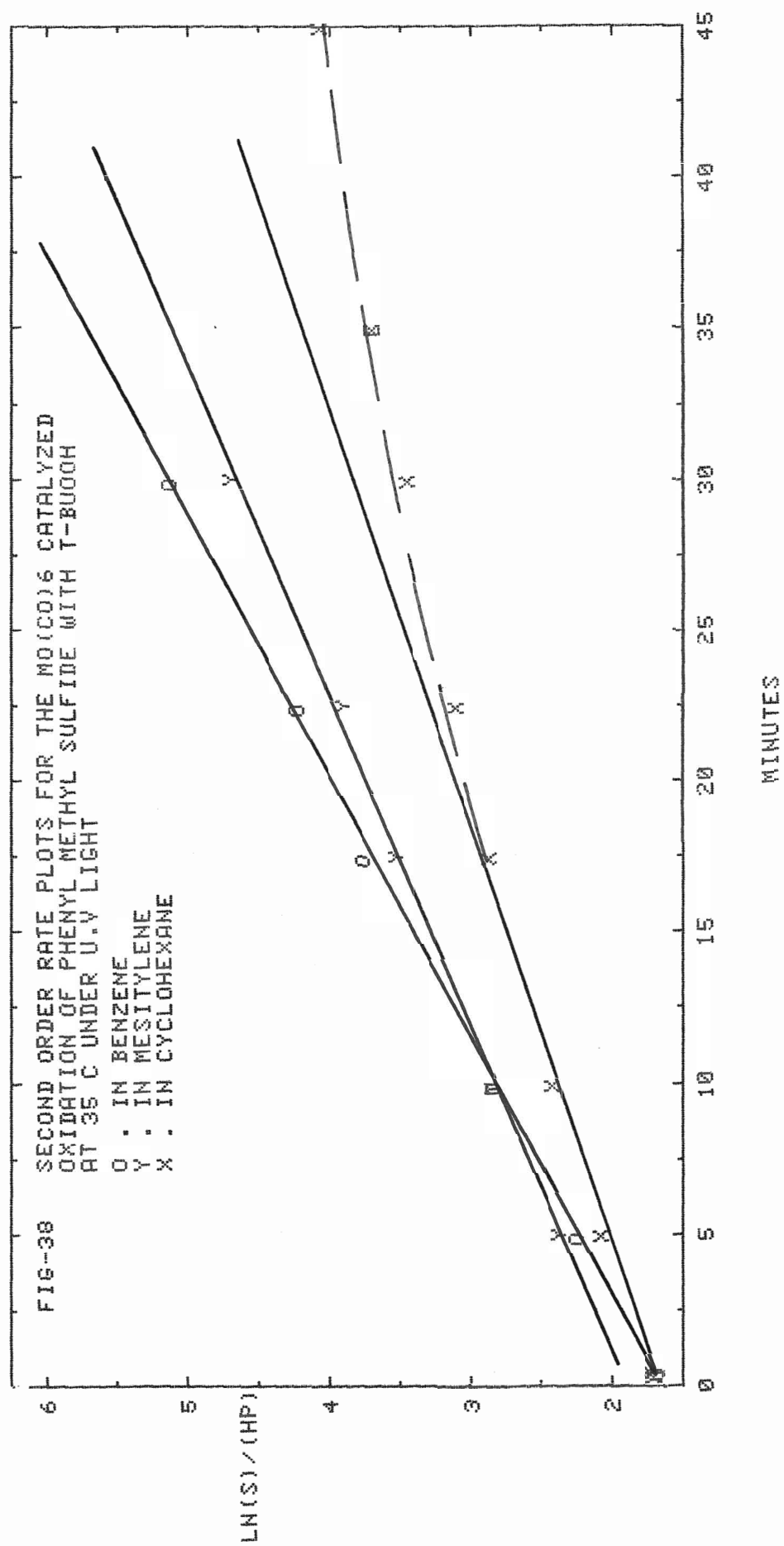
As reported by Bateman and Hargrave (73), the reaction order was found to be second order in hydroperoxide and first order in sulfide in the oxidation of cyclohexylmethyl sulfide by $t\text{-BuO}_2\text{H}$ in both benzene and cyclohexane. This indicates that the transition state contains two molecules of hydroperoxides.

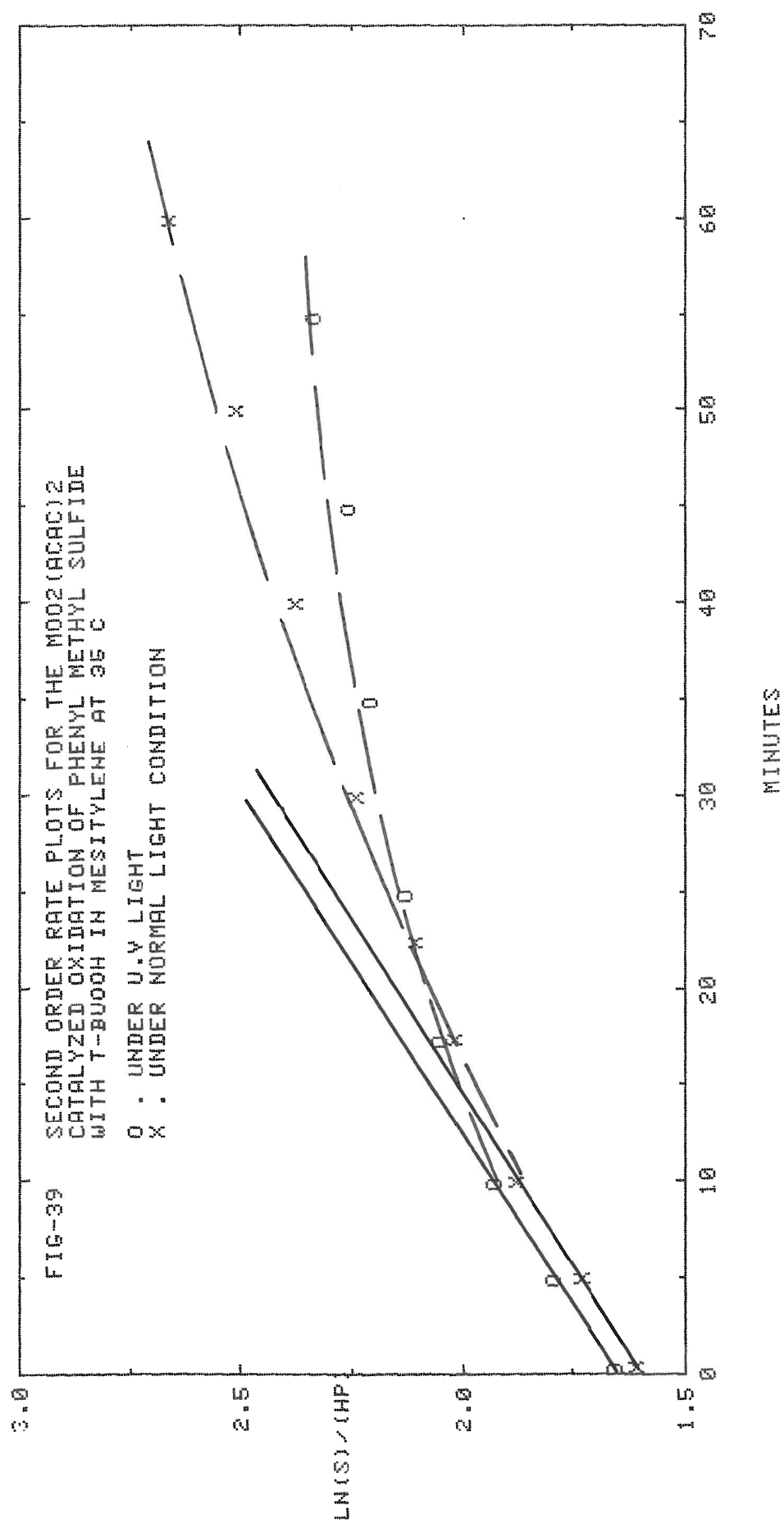
Kinetic studies in this work showed that a deviation was observed from the second order rate plot (Fig. 38) of the Mo(CO)_6 -catalyzed $t\text{-BuO}_2\text{H}$ oxidation of phenylmethyl sulfide in cyclohexane; slight deviations were also observed for reactions in benzene and mesitylene. Detailed kinetic studies are needed to find the actual reaction orders. These deviations were actually due to the involvement of the second hydroperoxide molecule in the transition state. The rate constants were, however, calculated from the second order rate plot. In the case of cyclohexane, the first four points were used to calculate the rate constants.

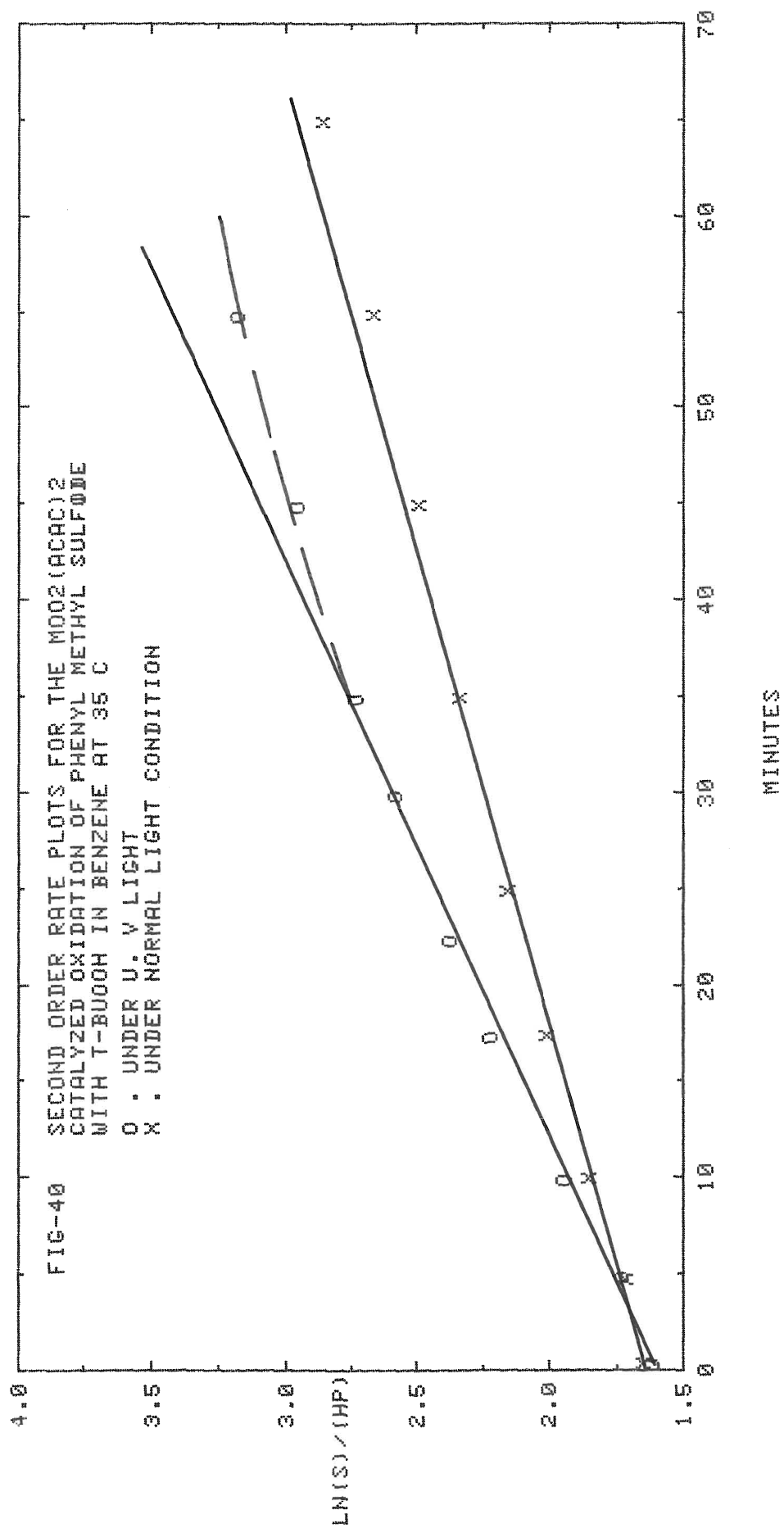
If the hydrogen transfer in the transition state was promoted by the second molecule of $t\text{-BuO}_2\text{H}$, when cyclohexane, benzene and mesitylene were employed as solvents, the reactions should proceed at the same rate, but they do not. On the contrary, the reactions proceeded more slowly in cyclohexane than in benzene or mesitylene. This can be explained by the electrophilic nature of benzene and mesitylene. It is very difficult to ascribe the complexation of solvents with catalyst with these results.

Similar deviations from the second order rate plot (Figs. 39, 40) were also observed in the $\text{MoO}_2(\text{acac})_2$ -catalyzed systems under both light conditions. More deviations, however, were observed for the UV radiated reactions. The behaviour of the solvents can be best explained by the









intervention of a second hydroperoxide molecule in the transition state and competition between the solvent, hydroperoxides and sulfides to complex with the catalyst because of more deviations from the second order rate plot on the UV radiated reactions.

As expected, the reactions in ethanol are straightforward. More detailed experiments are needed to find the actual reaction orders and to investigate the effect of solvents by using a number of solvents.

It can be concluded that ethanol is the best solvent in the $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation under both light conditions, as is benzene in the $\text{Mo}(\text{CO})_6$ -catalyzed oxidation under UV radiation.

VIII. The oxidation of diphenyl sulfoxide

Little work has been done on the metal-catalyzed oxidation of sulfoxides to sulfones by $t\text{-BuO}_2\text{H}$, even though detailed kinetic and mechanistic studies have been done on the oxidation of sulfides (5, 38-44, 46).

It is known that diphenyl sulfoxide is unreactive in the Mo(CO)_6 -catalyzed $t\text{-BuO}_2\text{H}$ oxidation at 35°C (46). whereas diphenyl sulfoxide showed reactivity with $k_3 = 1.55 \text{ M}^{-2} \text{ min}^{-1}$ in the presence of excess sulfide. The VO(acac)_2 -catalyzed oxidation of diphenyl sulfoxide was also reported (46).

The oxidation of diphenyl sulfoxide was studied to explore its activity using Mo(CO)_6 , $\text{MoO}_2(\text{acac})_2$ and VO(acac)_2 as catalysts under various light conditions. Since there is no decomposition of $t\text{-BuO}_2\text{H}$, the reactions were followed by monitoring the disappearance of $t\text{-BuO}_2\text{H}$ by iodometric titration. All reactions follow second order kinetics (Figs. 39-43); kinetic results are listed in Table 15.

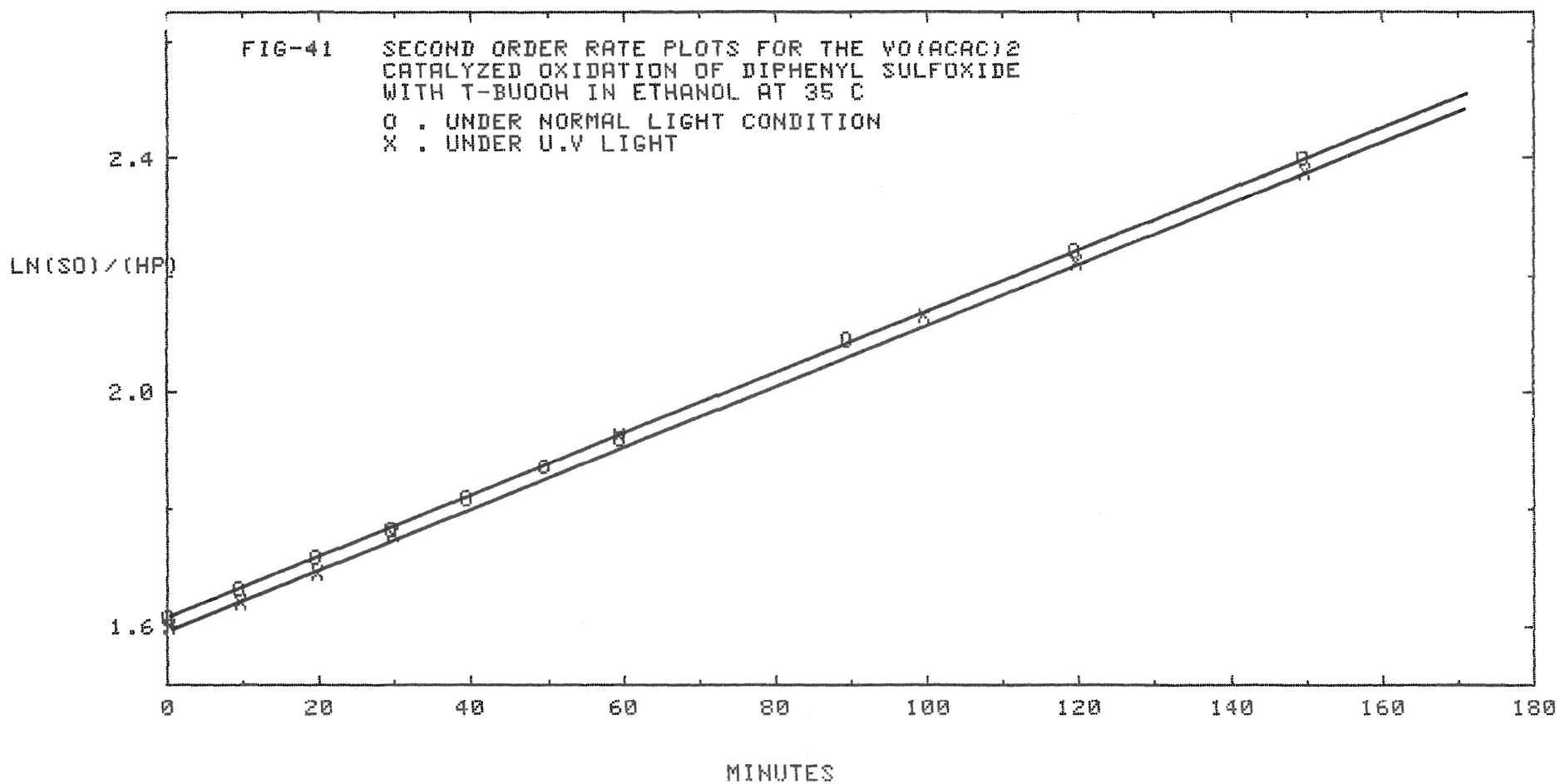
It is difficult to say whether UV light has an influence on the $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation reactions since the rate constants do not differ greatly from each other under various light conditions. The differences between the rate constants may be due to experimental error.

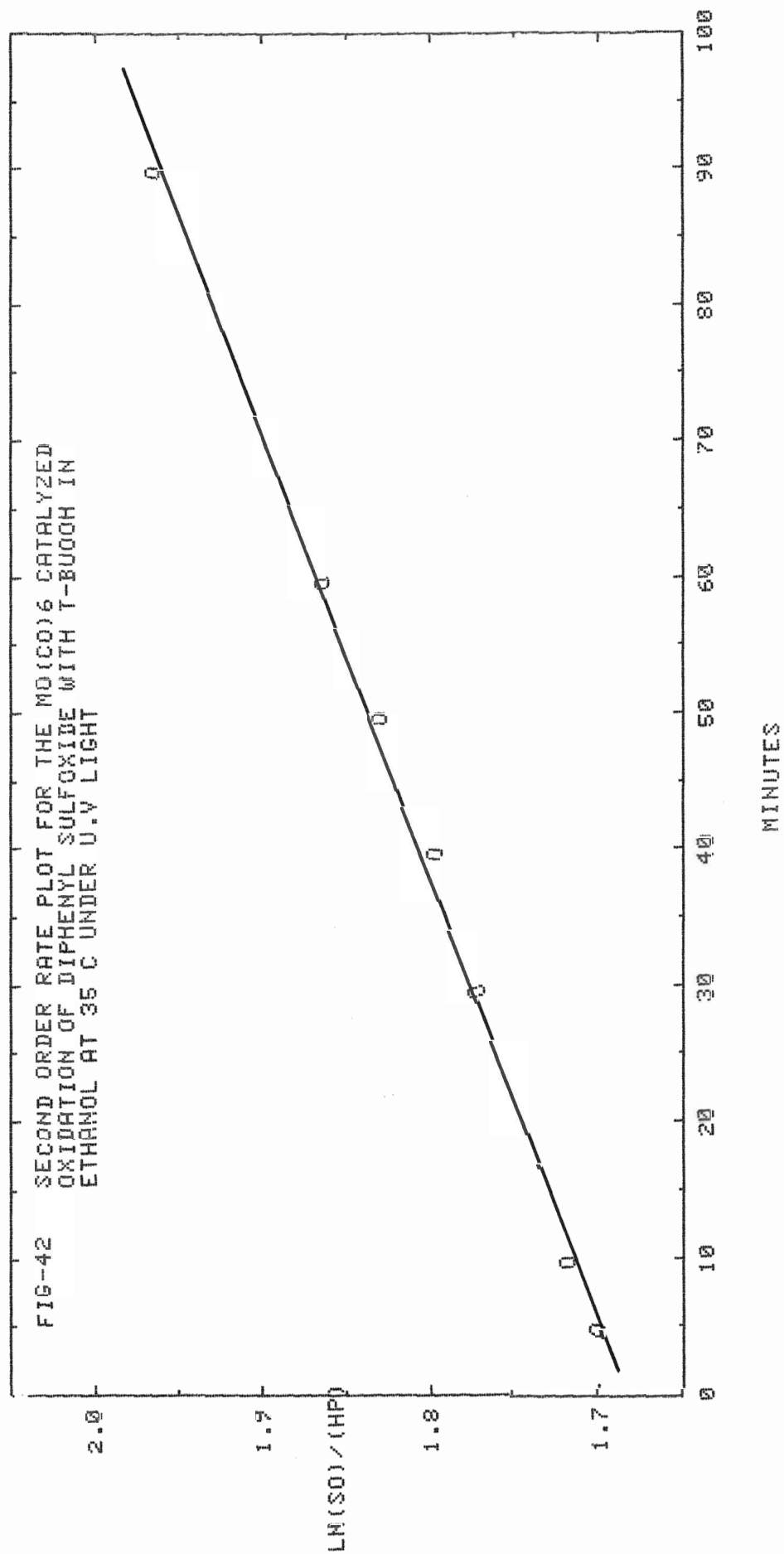
Oxidations catalyzed by VO(acac)_2 proceed faster than those catalyzed by Mo(CO)_6 and $\text{MoO}_2(\text{acac})_2$ complexes. Similar to $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidations, UV light does not affect the rate of oxidation. However, UV light does affect the oxidation rate in the Mo(CO)_6 -catalyzed oxidation. As in the sulfide oxidation, UV light and $t\text{-BuO}_2\text{H}$ play an important role

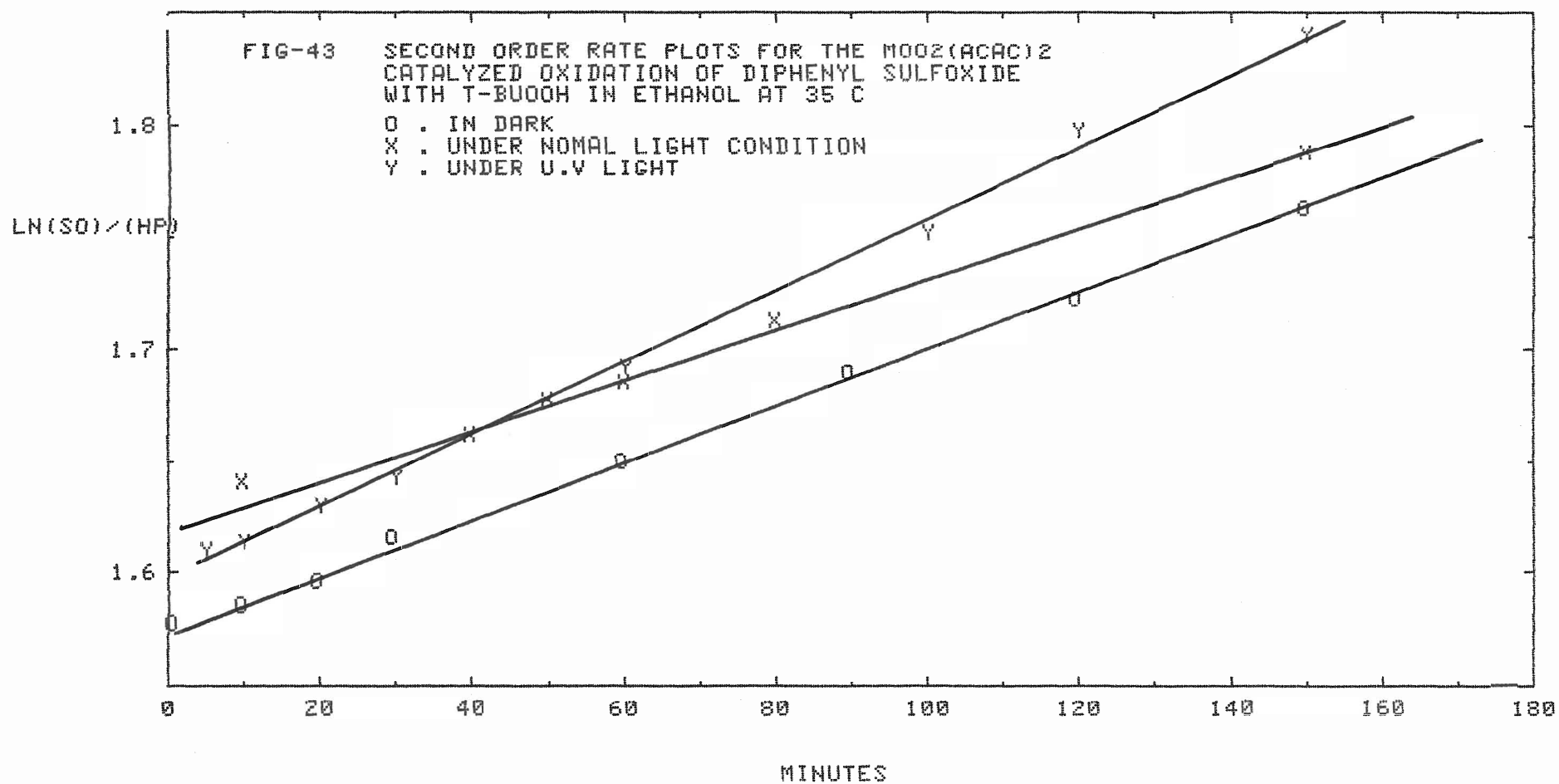
Table 15. The oxidation of diphenyl sulfoxide with t-BuO₂H in the presence of Mo(CO)₆, MoO₂(acac)₂ and VO(acac)₂ under various light conditions.^a

Run Number	[Ph ₂ SO]	[t-BuO ₂ H]	Catalyst	[cat] x 10 ⁵	Light Conditions	k ₂ x 10 ³ M ⁻¹ min ⁻¹	k ₃ M ⁻² min ⁻¹
94	1.004	0.2094	MoO ₂ (acac) ₂	402.7	dark	1.57	0.391
61	1.004	0.2024	MoO ₂ (acac) ₂	402.3	normal	1.35	0.337
159	0.9992	0.2066	MoO ₂ (acac) ₂	407.2	UV	2.04	0.499
82	1.006	0.2070	VO(acac) ₂	409.8	normal	6.63	1.62
160	1.000	0.2066	VO(acac) ₂	409.4	UV	6.65	1.62
145	1.005	0.2050	Mo(CO) ₆	401.0	UV	3.80	0.953

^a at 35°C, under air atmosphere, in ethanol.







in the activation of the catalyst. The smaller value of k_3 in the absence of diphenyl sulfide indicates that sulfide is the second factor in the oxidation reactions as a co-catalyst.

CONCLUSION

From the kinetic and spectroscopic evidence, it appears that the catalytic activities of Mo(CO)_6 and $\text{MoO}_2(\text{acac})_2$, in the reaction of $t\text{-BuO}_2\text{H}$ with organic sulfides and olefins are best explained by the formation of the Mo(VI) species.

The discovery of the light effect on the oxidation reaction provides another tool for investigating the formation of the Mo(VI) species. In the Mo(CO)_6 -catalyzed oxidation, hydroperoxide and radiation, or hydroperoxide and heat are required to activate the catalyst, whereas, at low temperatures and under normal laboratory lighting, hydroperoxide alone is able to partially convert Mo(CO)_6 to Mo(VI) . Any slight changes in the lighting conditions of the reaction environment adversely affect the reproducibility, due to partial conversion of Mo(CO)_6 .

The kinetic data indicate that hydroperoxide itself is sufficient to convert $\text{MoO}_2(\text{acac})_2$ to a catalytically active species.

The substituent effect on the $\text{MoO}_2(\text{acac})_2$ -catalyzed oxidation is as expected. Three values of the reaction constant (ρ) gave the same correlation by using σ , σ^- and σ^* constants. The use of σ^* constants is reasonable due to the similar electronic structures of sulfides and thiols.

The competitive reactions are indicative of co-catalytic activity of sulfides in the molybdenum-catalyzed reactions.

The solvent effect on the oxidation reaction is explained by the involvement of the second hydroperoxide molecule in the transition state.

The complexation of solvents with the catalyst through π systems, however, could not be explained.

The reactivity of diphenyl sulfoxide, in the $\text{VO}(\text{acac})_2$ and $\text{MoO}_2(\text{acac})_2$ catalyzed systems, under UV light or normal laboratory lighting, showed that catalytically active species can form with hydroperoxide; however, the reactivity of diphenyl sulfoxide under UV light and the non-reactivity of diphenyl sulfoxide under normal laboratory lighting is additional evidence of the catalyst activation.

Finally, it can be concluded that the effect of light on the molybdenum-catalyzed oxidations is an important factor, and the co-catalytic activity of sulfide is interesting.

REFERENCES

1. N. Indictor and W. F. Brill, J. Org. Chem. 30, 2074 (1965).
2. M. N. Sheng and J. C. Zajacek, Adv. in Chem. Series 76, 418 (1968).
3. R. A. Sheldon and J. A. V. Doorn, J. Cat. 31, 427 (1973).
4. V. A. Gavrilenko, E. I. Evzerikhin, V. A. Kolosov, G. M. Larin and I. I. Moiseev, Izv. Ak. Nauk. SSSR Ser. Khim. 9, 1877 (1974).
5. R. Curci, F. Di Furia, R. Testi and G. Modena, J. Chem. Soc. Perkin II 752 (1974).
6. R. B. Svitych, A. L. Buchachenko, O. P. Yablonski, A. A. Petukhov, V. A. Belyaev and A. K. Koloyakov, Kinetics and Catalysis 15, 1149 (1974).
7. R. B. Svitych, A. L. Buchachenko, O. P. Yablonski, N. N. Rzhetskaya, V. A. Belyaev and A. A. Petukov, Kinetics and Catalysis 15, 60 (1976).
8. I. P. Skibida and P. Kok, Izv. Ak. Nauk. SSSR Ser. Khim. 12, 2599 (1974).
9. M. N. Sheng and J. C. Zajacek, J. Org. Chem. 35, 1839 (1970).
10. E. S. Gould, K. C. Irwin and R. R. Hiatt, J. Am. Chem. Soc. 90, 4573 (1968).
11. C. C. Su, J. W. Reed and E. S. Gould, Inorg. Chem. 12, 337 (1973).
12. R. A. Sheldon, Recl. Trav. Chim. Pays-Bas 92, 253 (1973).
13. R. A. Sheldon, Recl. Trav. Chim. Pays-Bas 92, 369 (1973).
14. R. R. Hiatt and G. Howe, J. Org. Chem. 36, 2493 (1971).
15. V. N. Sapunov, I. Margitfal'vi and N. N. Lebedev, Kinetics and Catalysis 15, 1046 (1974).
16. V. N. Sapunov, I. Margitfal'vi and N. N. Lebedev, Kinetics and Catalysis 15, 1274 (1974).
17. R. A. Sheldon, J. A. V. Doorn, C. W. A. Schram and A. J. De Jang, J. Cat. 31, 438 (1973).

18. V. N. Sapunov, I. Margitfal'vi and N. N. Levedev, *Kinetics and Catalysis* 15, 1051 (1974).
19. V. N. Sapunov, T. A. Margitfal'vi and I. Morgitfal'vi, *Kinetics and Catalysis* 15, 1278 (1974).
20. V. N. Sapunov, I. Yu Litvintsev, R. B. Svitych and N. N. Rzhetskaya, Deposited Doc. 1976 VINITI 1446-76; Chem. Abs. 88: 135909r.
21. V. N. Sapunov, I. Yu Litvintsev, I. Margitfal'vi and N. N. Lebedev, Deposited Doc. 1976 VINITI 1447-76; Chem. Abs. 88: 5009x.
22. V. N. Sapunov, I. Yu Litvintsev, G. I. Magamedev and I. Margitfal'vi, Deposited Doc. 1976 VINITI 1451-6; Chem. Abs. 88: 61797d.
23. V. N. Sapunov, I. Yu Litvintsev and V. G. Sharykin, *Izv. Vyssh. Uchebu. Zaved. Khim. Khim. Tekhnol.* 1978, 21 (11), 1583-6; Chem. Abs. 91: 19458f.
24. V. N. Sapunov and I. Yu Litvintsev, Deposited Doc. 1978 VINITI 322-78; Chem. Abs. 91: 156988t.
25. V. N. Sapunov, I. A. Krylov and S. P. Laurova, *Tr. Mosk. Khim. Tekhnol. ins. im. D. I. Mendeleeva*, 99, 112-117 (1978).
26. J. Sobczak and J. J. Ziolkowski, *Inorg. Chim. Acta* 19, 15 (1976).
27. L. Sumgei and Yu D. Norikov, *React. Kinet. Catal. Lett.* 11(4), 365-370 (1979).
28. I. Stovikova and E. J. Mistrik, *Petrochemia* 1978, 18(5-6), 186-192; Chem. Abs. 91: 56716j.
29. M. I. Farberov, L. V. Mel'nik, B. N. Bobylev and V. A. Podgornova, *Kinetics and Catalysis* 12, 1018 (1971).
30. K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.* 95, 6136 (1973).
31. Shin Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson and J. D. Cutting, *J. Am. Chem. Soc.* 96, 5254 (1974).
32. B. E. Rossiter, T. R. Verhoeven and K. B. Sharpless, *Tetrahedron Letters* 49, 4733 (1979).
33. K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta* 12, 63 (1979).
34. R. R. Hiatt and C. McColeman, *Can. J. Chem.* 49, 1712 (1971).

35. R. R. Hiatt, C. McColeman and G. R. Howe, *Can. J. Chem.* 53, 559 (1975).
36. G. R. Howe and R. R. Hiatt, *J. Org. Chem.* 35, 4007 (1970).
37. M. N. Sheng and J. C. Zajacek, *J. Org. Chem.* 33, 588 (1968).
38. R. Curci, F. Di Furia and G. Modena, *J. Chem. Soc. Perkin II* 576 (1976).
39. S. Cenci, F. Di Furia and G. Modena, *J. Chem. Soc. Perkin II* 979 (1978).
40. F. Di Furia and G. Modena, *Gazz. Chim. Ital.* 108, 639 (1978).
41. F. Di Furia and G. Modena, *Recl. Trav. Chim. Pays-Bas* 98, 181 (1979).
42. F. Di Furia, G. Modena, R. Curci and J. O. Edwards, *Gazz. Chim. Ital.* 109, 571 (1979).
43. F. Di Furia, G. Modena, R. Curci and J. O. Edwards, *J. Chem. Soc. Perkin II* 457 (1980).
44. F. Di Furia, G. Modena, R. Curci and J. O. Edwards, *Gazz. Chim. Ital.* 110, 4871 (1980).
45. G. Modena and L. Maioli, *Gazz. Chim. Ital.* 87, 673 (1957).
46. S. S. Köseoğlu, M.Sc. Thesis, Brock University, 1980.
47. G. Modena, *Gazz. Chim. Ital.* 87, 1306 (1957).
48. F. Trifiro, P. Forzatti, S. Preite and I. Pasquau, in "Chemistry and uses of molybdenum", ed. P. C. H. Mitchell, Climax Molybdenum Company Limited, London, 1968, pp. 169 ff.
49. P. J. White, J. M. Kaus, J. O. Edwards and P. H. Riegel, *J. Chem. Soc. Chem. Comm.* 429 (1976).
50. C. M. Suter and H. L. Hansen, *J. Am. Chem. Soc.* 54, 4100-4105 (1932).
51. C. C. Price and G. W. Stacy, *J. Am. Chem. Soc.* 68, 498-500 (1946).
52. F. G. Bardwell and P. J. Bouter, *J. Am. Chem. Soc.* 79, 717 (1957).
53. M. S. Newman and H. Karnes, *J. Org. Chem.* 31, 3980 (1966).
54. I. M. Carter, B.Sc. Thesis, Brock University, p. 23, 1981.

55. R. S. Monson, "Advanced Organic Synthesis Methods and Techniques", Academic Press, New York, 64, 1971.
56. J. H. Clark and J. M. Miller, J. Am. Chem. Soc. 99, 498 (1977).
57. N. J. Leonard and C. R. Johnson, J. Org. Chem. 27, 282-284 (1962).
58. E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw and B. C. Smith, J. Chem. Soc. 429 (1965).
59. W. Strohmeier, J. F. Guttenberger and G. Popp, Chem. Ber. 98, 2248 (1965).
60. L. E. Orgel, Inorg. Chem. 1, 25 (1962).
61. G. R. Dobson, M. F. A. Elsayed, I. W. Stolz and R. K. Sheline, Inorg. Chem. 1, 527 (1962).
62. I. W. Stolz, G. R. Dobson and R. K. Sheline, Inorg. Chem. 2, 232 (1963).
63. I. W. Stolz, G. R. Dobson and R. K. Sheline, Inorg. Chem. 2, 1264 (1963).
64. I. W. Stolz, G. R. Dobson and R. K. Sheline, J. Am. Chem. Soc. 84, 3589 (1962).
65. I. W. Stolz, G. R. Dobson and R. K. Sheline, J. Am. Chem. Soc. 85, 1013 (1963).
66. M. Herberhold and G. Süß, J. Chem. Research (S) 246 (1977), J. Chem. Research (M) 2720-2743 (1977).
67. F. G. Bardwell and H. M. Andersen, J. Am. Chem. Soc. 75, 6019 (1953).
68. G. Schwarzenback and H. Egli, Helv. Chim. Acta 17, 1176 (1934).
69. G. Schwarzenback and H. Egli, Helv. Chim. Acta 17, 1183 (1934).
70. G. Schwarzenback and E. Rudin, Helv. Chim. Acta 22, 360 (1939).
71. H. H. Jaffe, Chem. Rev. 53, 191 (1953).
72. J. O. Edwards, "Peroxide reaction mechanisms", John Wiley and Sons, New York, p. 67 (1962).

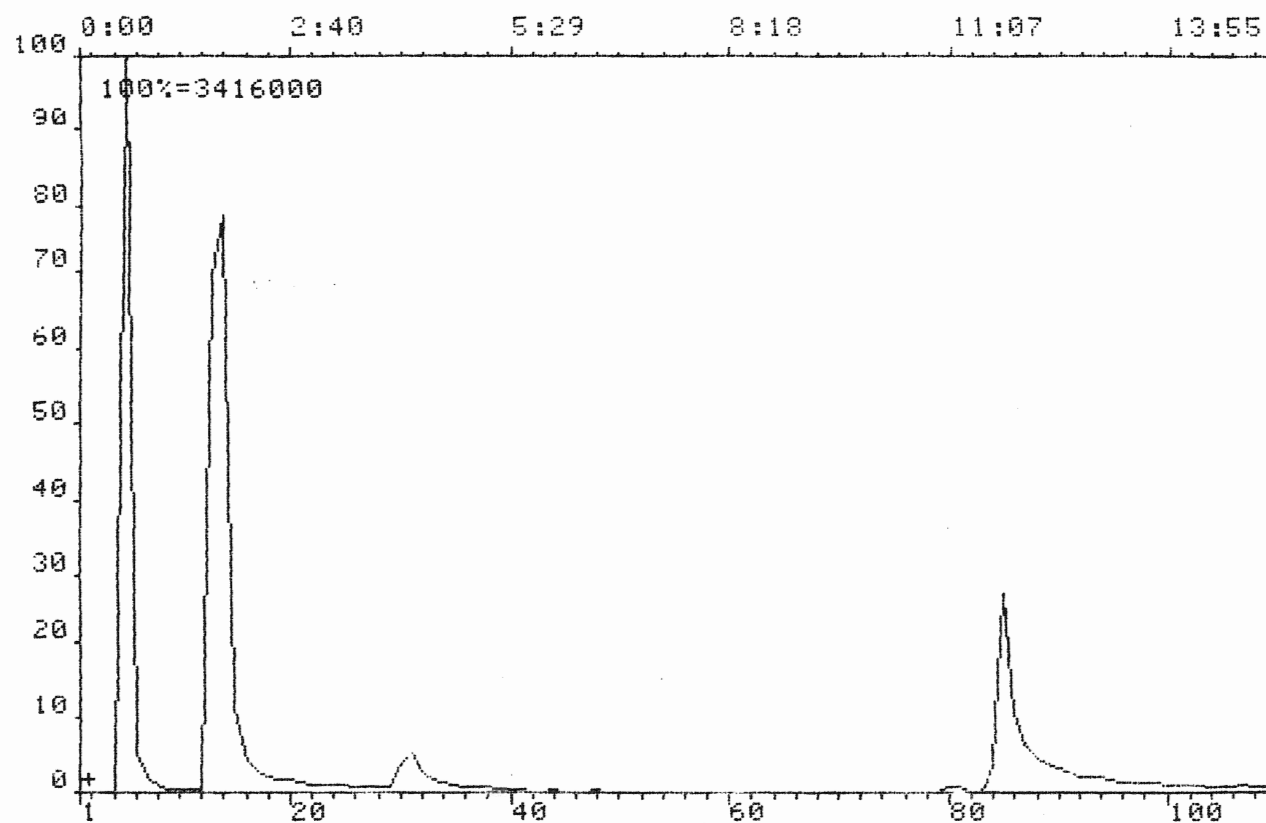
73. L. Bateman and K. R. Hargrave, Proc. Roy. Soc. A224, 289 (1954).

APPENDICES

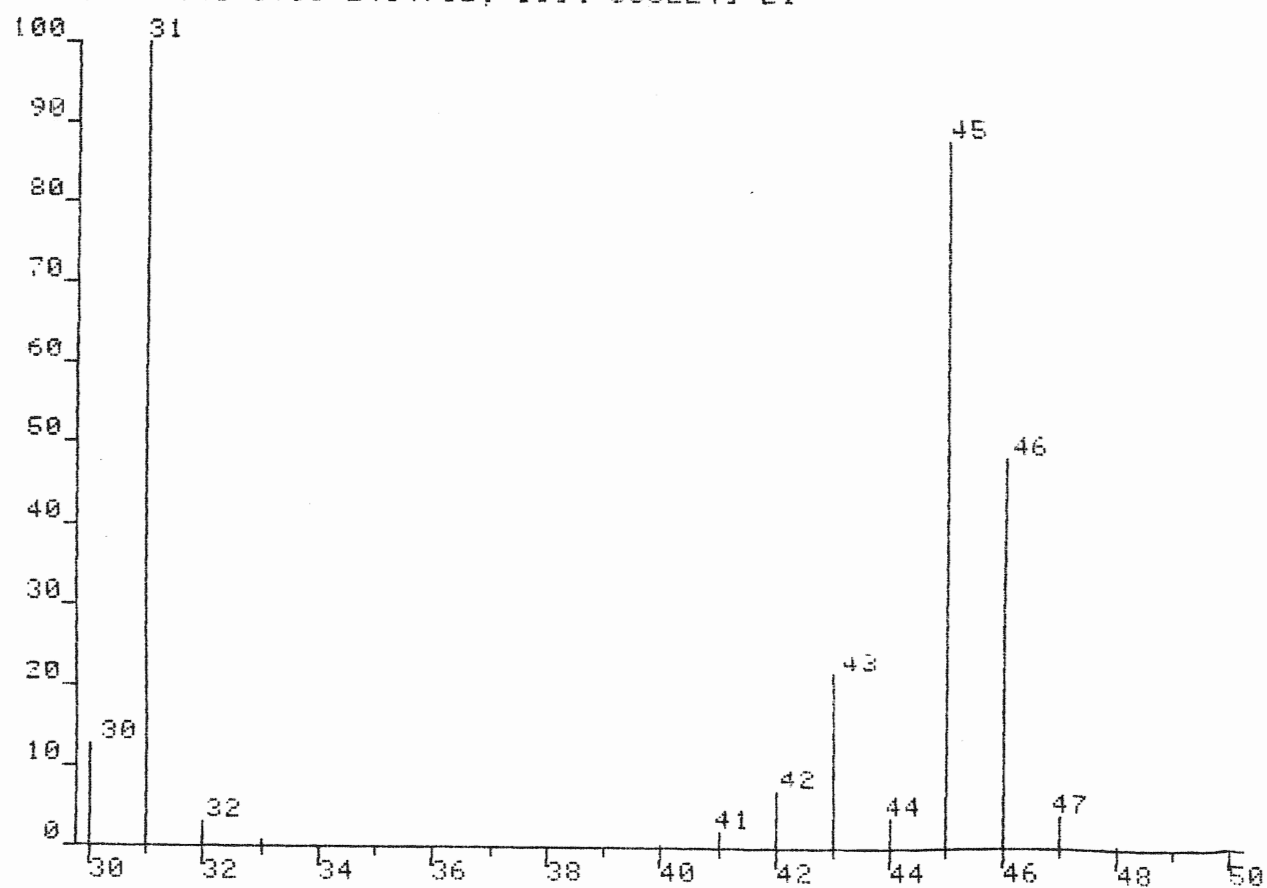
Appendix 1

The chromatogram and the mass spectra of the mixture of ethanol, triethylphosphite, triethylphosphate, diphenyl sulfide and diphenyl sulfoxide.

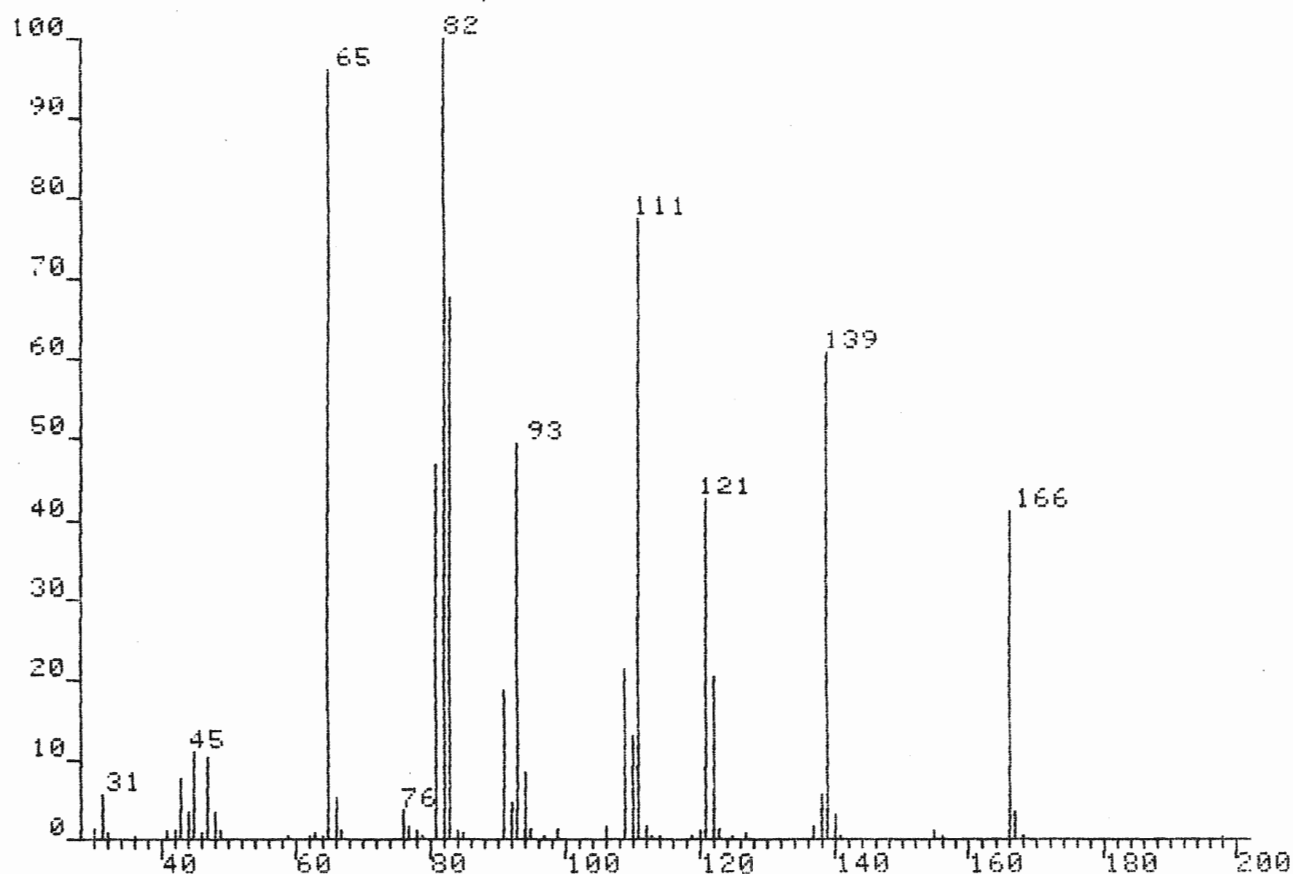
03-55 CROSS SCAN REPORT, RUN: 25REFA 500/2MIN., 200/MIN., -1800
+ TIC



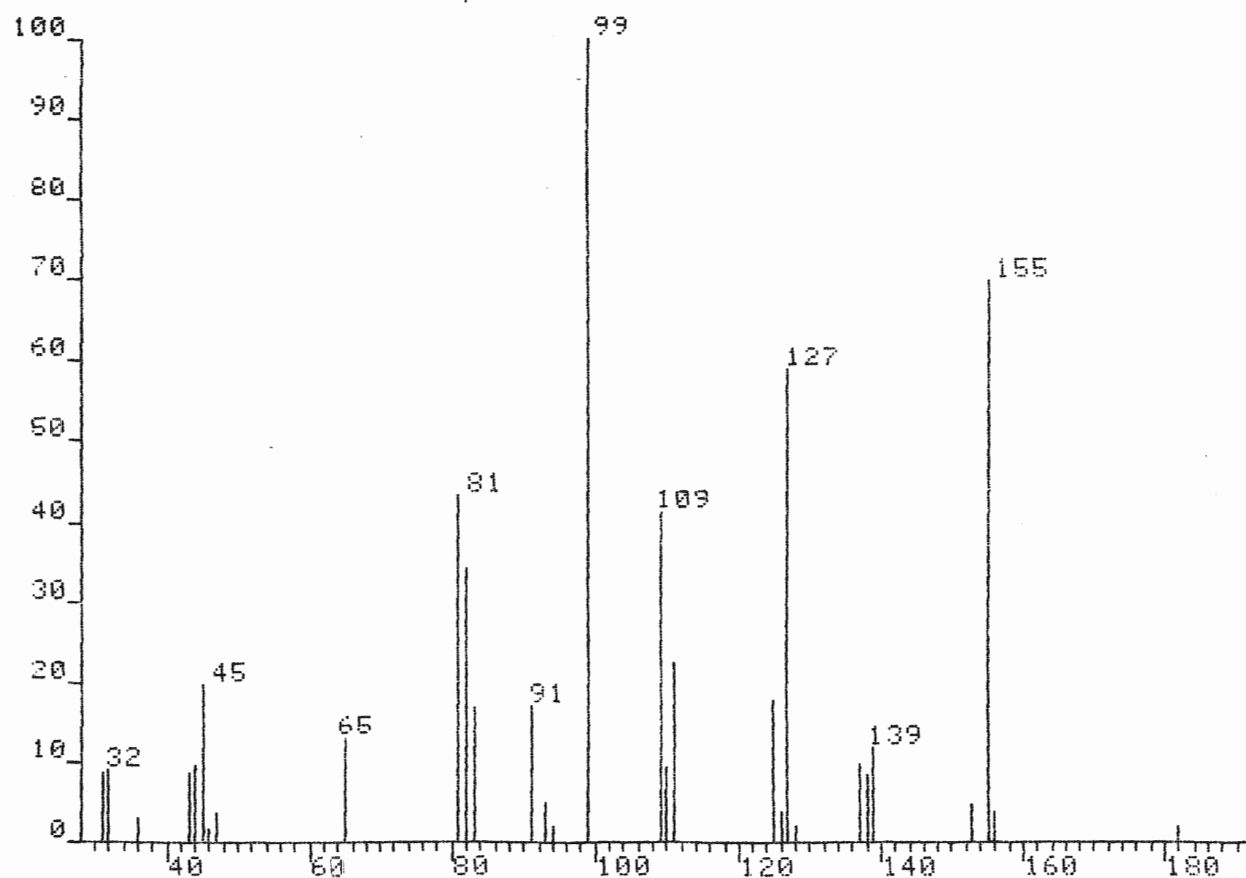
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25RF05.1 [TIC=2434752, 100%=836224] EI



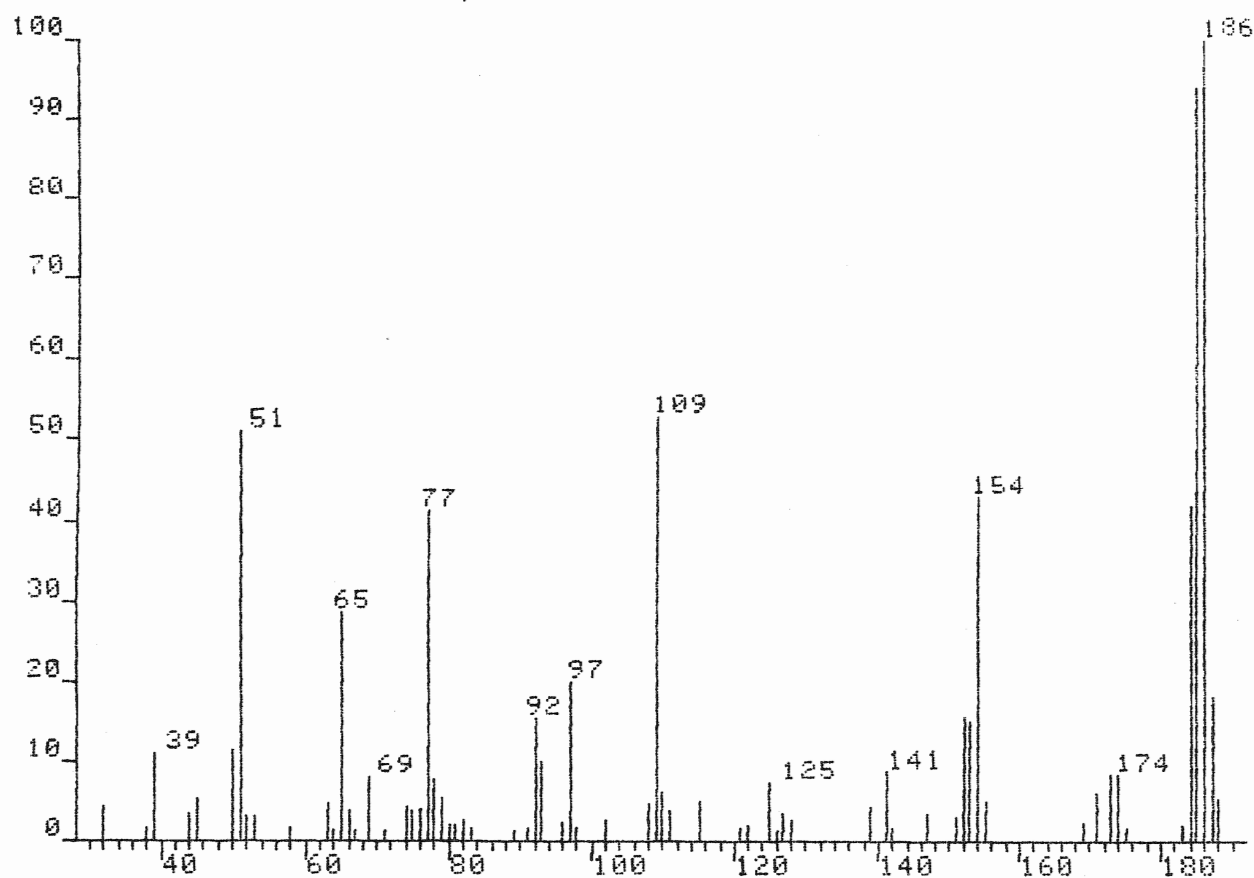
DS-55 MASS INTENSITY REPORT:
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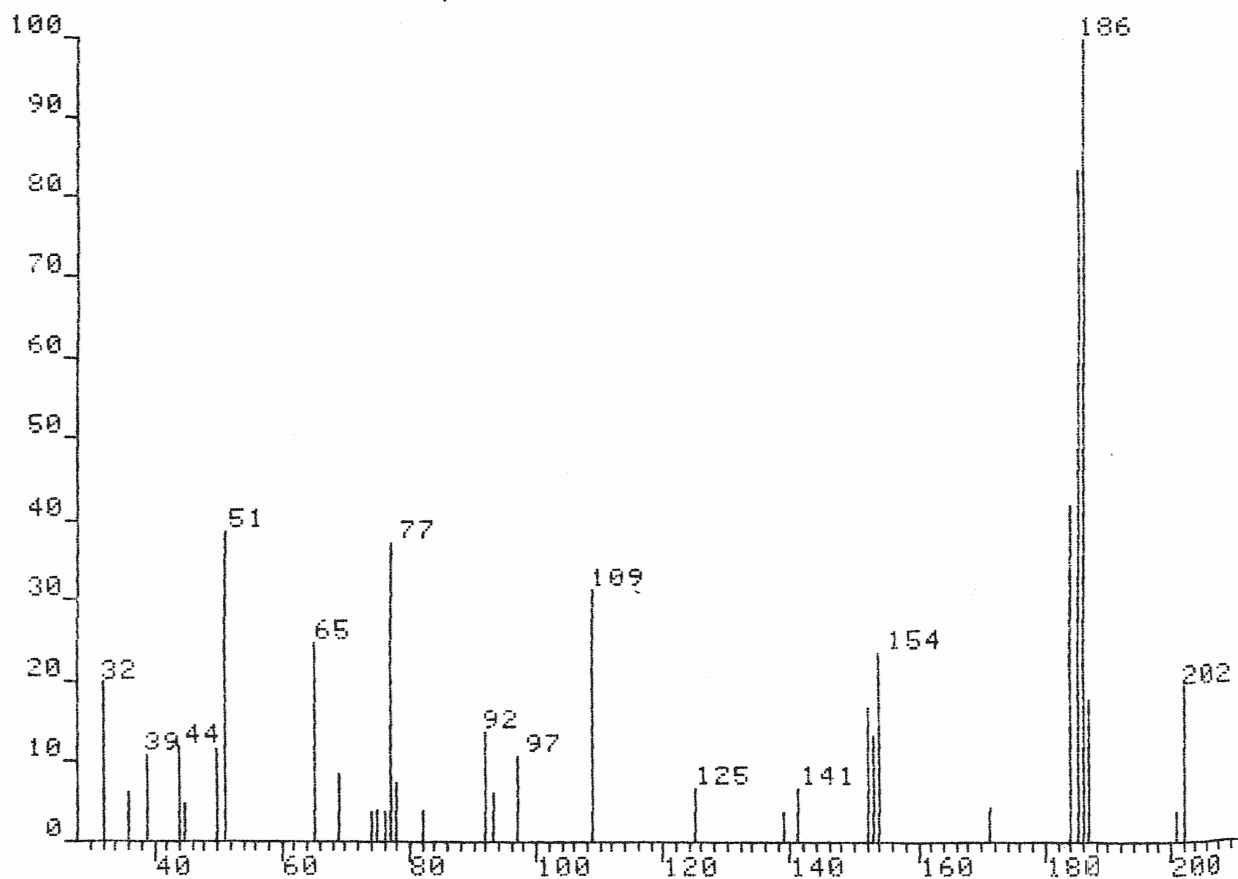
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25RF86.1 [TIC=343024, 100%=45945] EI



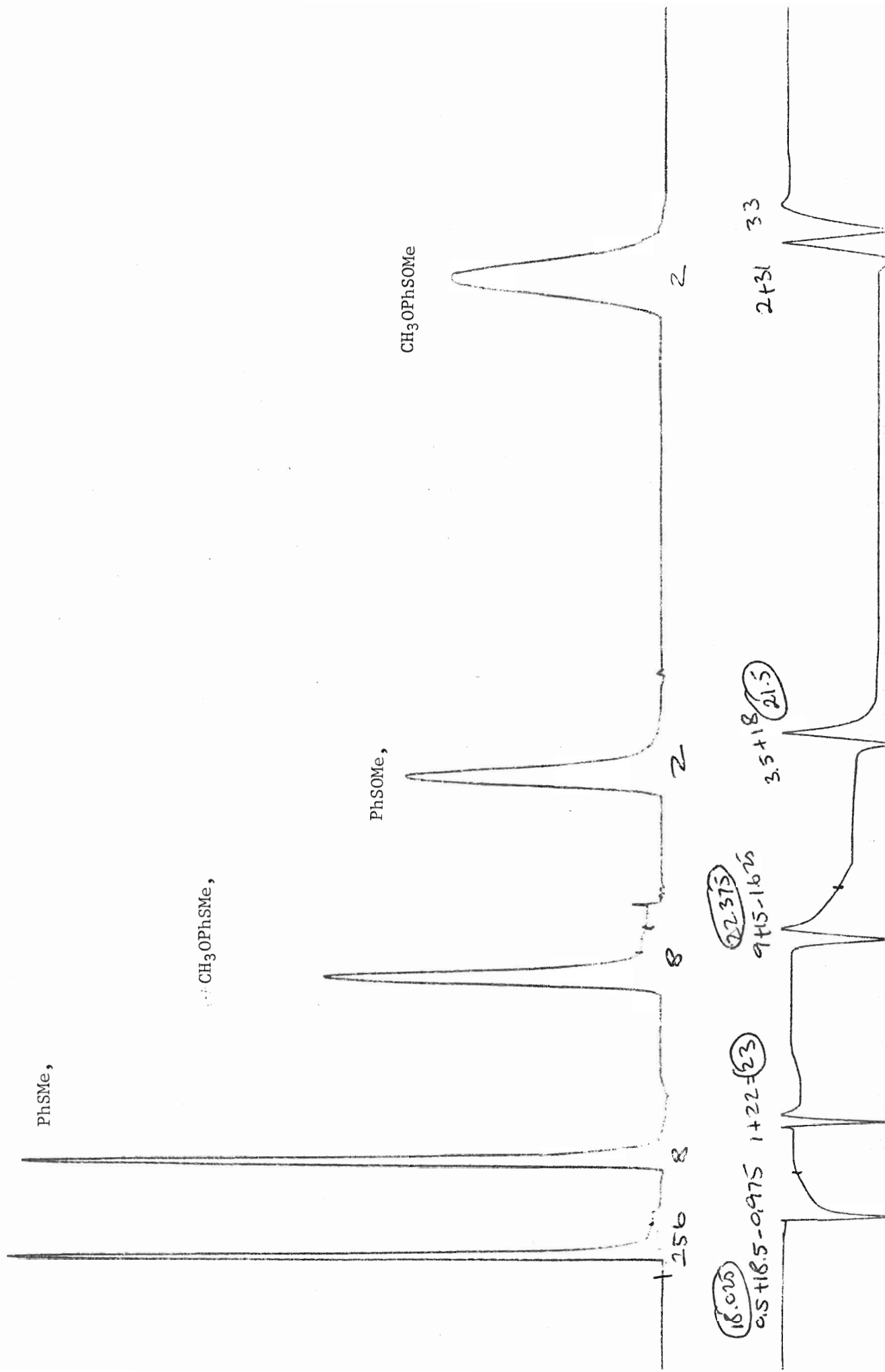
DS-55 MASS INTENSITY REPORT:
25RF92.1 [TIC=77048, 100%=12941] EI



APPENDIX 2

The chromatograms of the samples of the competitive reaction mixtures

EtOH,



EtOH,

PhSMe,

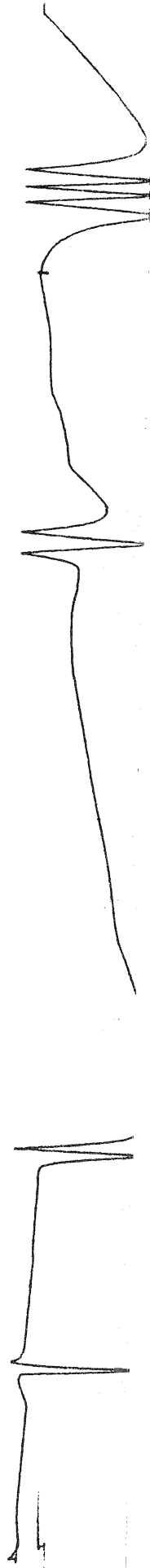
PhSOMe

NO₂PhSMe

252

4

4



Appendix 3

Extinction coefficients for methyl sulfoxide, p-nitrophenylmethyl sulfide and p-nitrophenylmethyl sulfoxide

Extinction coefficients for:

PhSMe	$\epsilon_{237} = 5306$	$\epsilon_{284} = --$
	$\epsilon_{254} = 10514$	$\epsilon_{340} = --$
PhSOMe	$\epsilon_{237} = 4119$	$\epsilon_{284} = --$
	$\epsilon_{254} = 1922$	$\epsilon_{340} = --$
MeOPhSMe	$\epsilon_{257} = 9737$	$\epsilon_{284} = 1271.91$
	$\epsilon_{243} = 6461.40$	$\epsilon_{340} = --$
MeOPhSOMe	$\epsilon_{257} = 2859$	$\epsilon_{284} = 86.35$
	$\epsilon_{243} = 9244.17$	$\epsilon_{340} = --$
NO ₂ PhSMe	$\epsilon_{237} = 5266.73$	$\epsilon_{340} = 13842.12$
	$\epsilon_{254} = 2531.58$	$\epsilon_{284} = 1643.89$
	$\epsilon_{257} = 1929.91$	
	$\epsilon_{243} = 4460.76$	
NO ₂ PhSOMe	$\epsilon_{237} = 5680.65$	$\epsilon_{284} = 5911$
	$\epsilon_{254} = 5583.17$	$\epsilon_{340} = 495.12$
	$\epsilon_{257} = 5254.35$	
	$\epsilon_{243} = 6047.66$	

Concentrations

$$\begin{array}{lll}
 c_1 = [\text{PhSMe}] & c_3 = [\text{MeOPhSMe}] & c_5 = [\text{NO}_2\text{PhSMe}] \\
 c_2 = [\text{PhSOMe}] & c_4 = [\text{MeOPhSOMe}] & c_6 = [\text{NO}_2\text{PhSOMe}]
 \end{array}$$

Equations

e.g., For H and NO₂-substituted sulfides and sulfoxides,

$$\text{OD}_{254} = c_1 \epsilon_{\text{PhSMe}} + c_2 \epsilon_{\text{PhSOMe}} + c_5 \epsilon_{\text{NO}_2\text{PhSMe}} + c_6 \epsilon_{\text{NO}_2\text{PhSOMe}}$$

$$\text{OD}_{340} = c_1 \epsilon_{\text{PhSMe}} + c_2 \epsilon_{\text{PhSOMe}} + c_5 \epsilon_{\text{NO}_2\text{PhSMe}} + c_6 \epsilon_{\text{NO}_2\text{PhSOMe}}$$

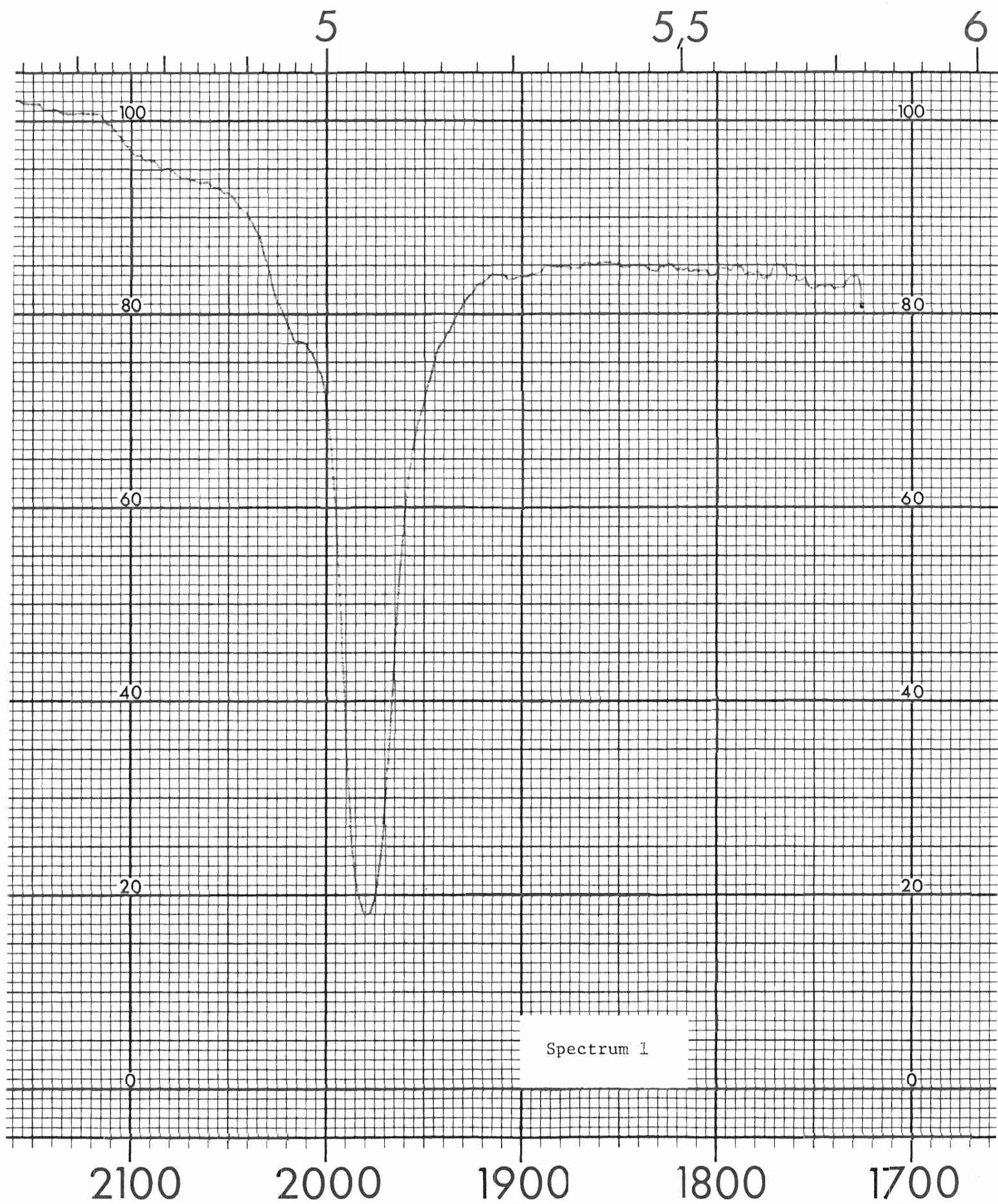
$$\text{Since } c_1 + c_2 = [\text{PhSMe}]_{\text{initial}}$$

$$c_5 + c_6 = [\text{NO PhSMe}]_{\text{initial}}$$

The unknowns can be reduced to two from four.

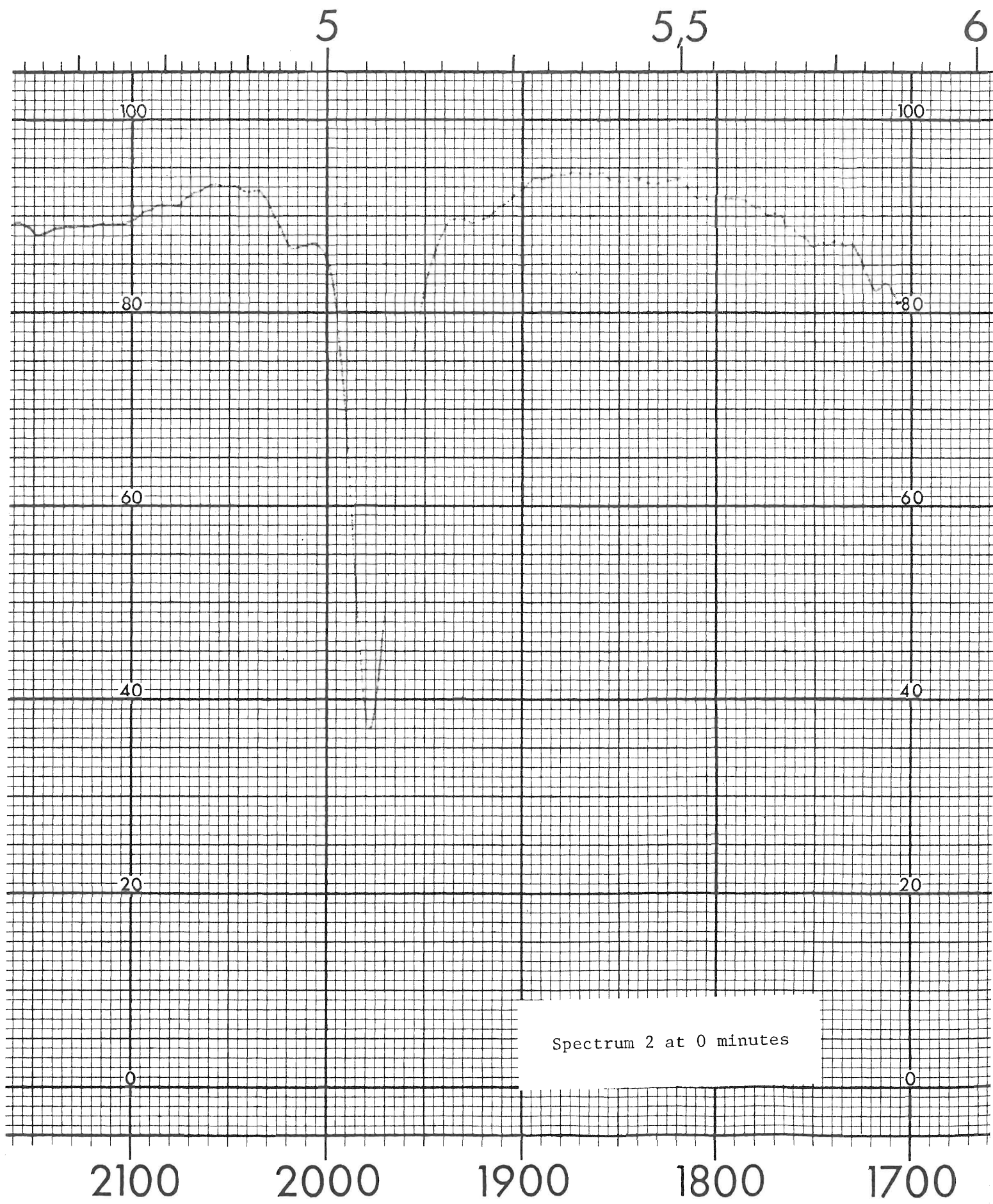
Appendix 4

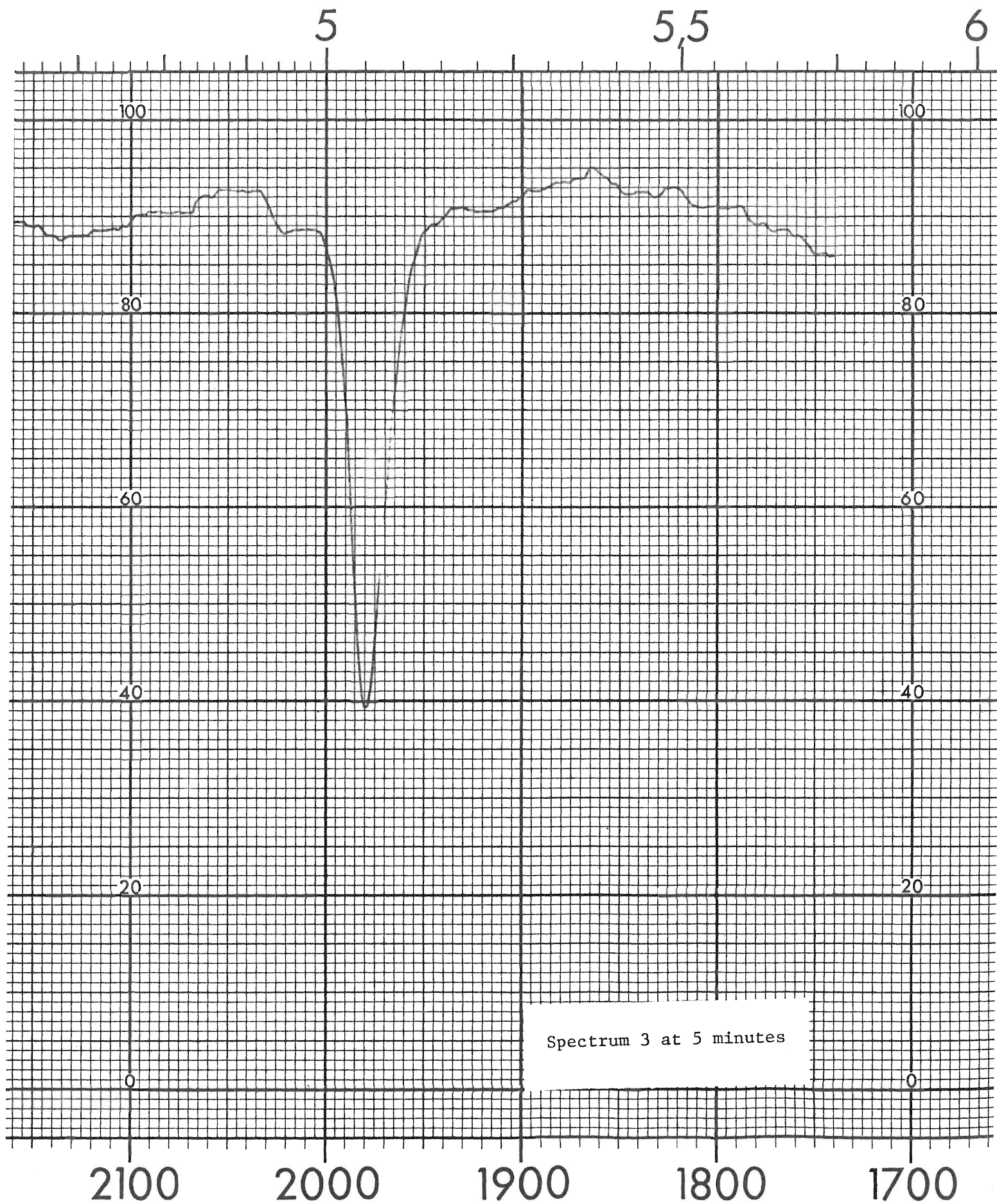
IR spectrum of Mo(CO)_6 in ethanol at 20°C

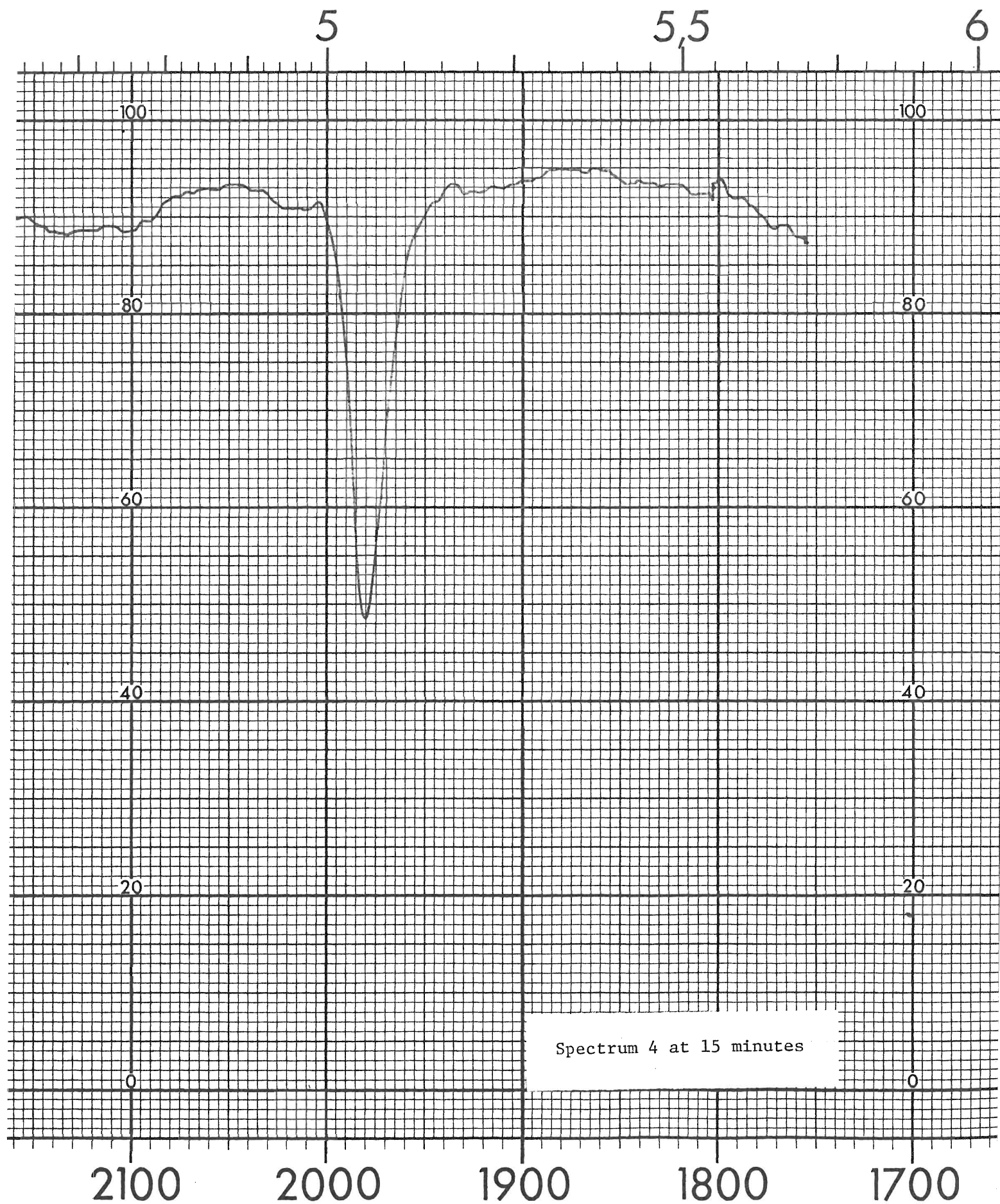


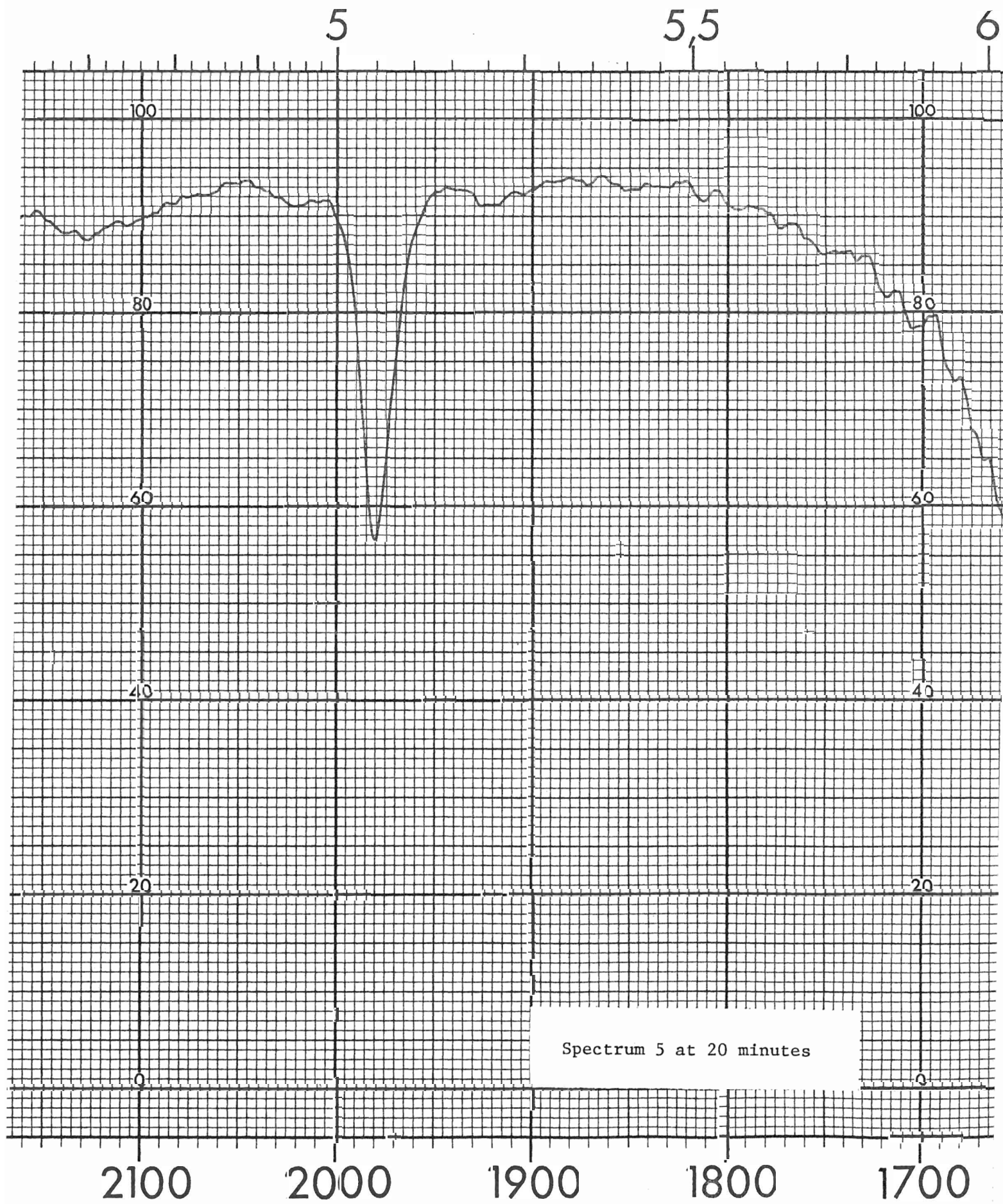
Appendix 5

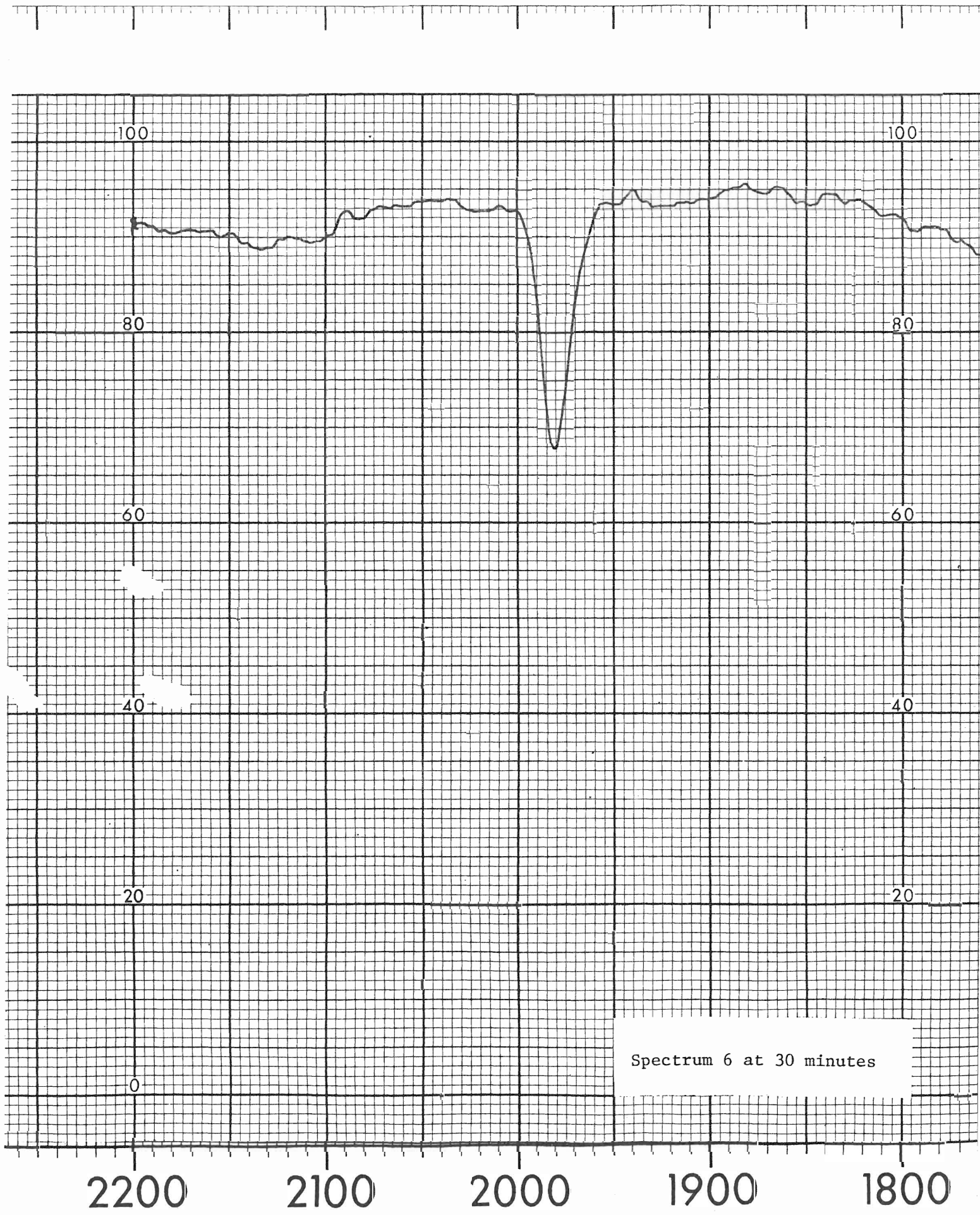
IR spectra of Mo(CO)_6 in the presence of $t\text{-BuO}_2\text{H}$ in ethanol at 20°C
at 0-30 minutes











Spectrum 6 at 30 minutes

Appendix 6

IR spectra of Mo(CO)_x -1-octene under various conditions and 1-octene
in the region of 2100-1700 cm^{-1}

